CHAPTER ONE

The application potential of coal fly ash for selenium biofortification

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Abstract

Combustion of coal in thermal power plants generates huge quantities of coal fly ash (CFA) worldwide. CFA contains a series of plant-essential elements, and one distinct beneficial reuse option of CFA is its utilization as a soil amendment. Applying CFA to soil at appropriate rates can improve soil physicochemical properties, thereby enhancing plant growth and crop yields. Most CFAs are richer in selenium (Se) than non-seleniferous soils; using Se-rich CFA for soil amendment can increase the bioavalabily of Se in soil and enhance Se uptake by plants. Plant material rich in Se produced on CFA-amended soils can be blended with low-Se material in a diet or used as dietary supplementation to provide sufficient Se for those humans suffering Se-deficiency. Therefore, it is promising to use CFA as a soil amendment for Se biofortification to address the Se-deficiency issue in vast numbers of people worldwide. In this chapter, we survey and describe the concentration and speciation of Se in CFA, summarize factors affecting Se mobility and bioavailability in CFA-amended soils, and plant uptake of Se from CFA-amended soils, and assess the effects of CFA application on Se accumulation by plants, plant growth and crop yield. We also list and discuss the disadvantages, potential negative effects and hazards associated with the application of CFA in agriculture, and propose a few measures for efficient use of CFA for Se biofortification and hazard reduction and prevention.

1. Introduction

Coal has been the largest source of electric power production in the world. Coal fly ash (CFA), a major by-product of coal-fired thermal power plants, is generated in huge quantities every year, and has become a problematic solid waste worldwide (Shaheen et al., 2014; Yao et al., 2015). Previously, disposal of CFA was mostly in landfill and disposal ponds, which has many deleterious effects on the ecosphere and becomes an environmental concern (Shaheen et al., 2014; Yao et al., 2015). A few economic and environmentally-sustainable alternative options for CFA disposal have been proposed and practiced, including the applications of CFA in construction industry, ceramic industry, zeolite synthesis, valuable metal recovery, depth separation, catalysis, and soil amendment. The global beneficial utilization

rate of CFA has been increasing recently (Blissett and Rowson, 2012; Jayaranjan et al., 2014; Shaheen et al., 2014; Yao et al., 2015), and about 41% of the CFA produced annualy worldwide is currently utilized (Hartuti et al., 2017).

One distinct beneficial reuse of CFA is its utilization in land application as a soil amendment (Jala and Goyal, 2006; Pandey and Singh, 2010; Shaheen et al., 2014). Compared with many soils, CFA has a finer texture, lower bulk density, higher water-holding capacity, favorable pH, and higher supply of a series of plant nutrients. When applied to the soil in appropriate amounts, CFA can improve the physicochemical properties of the soil, including soil texture, bulk density, water-holding capacity, pH, and supply of nutrients such as phosphorus (P), potassium (K), sulfur (S), iron (Fe), manganese (Mn), copper (Cu), zinc (Zn), molybdenum (Mo), and boron (B) (Blissett and Rowson, 2012; Jala and Goyal, 2006; Ram and Masto, 2014). Coal fly ash can be a valuable source of nutrient supplementation to improve soil fertility for reclamation and revegetation in disturbed areas, e.g., areas affected by surface mining (Bisoi et al., 2017; Pandey et al., 2009b; Ram and Masto, 2010), and to improve crop production as well (Jala and Goyal, 2006; Singh et al., 2010; Ukwattage et al., 2013; Yunusa et al., 2012). A number of studies have demonstrated that applying CFA to soils at appropriate rates enhances plant growth and increases yield of various crops, and increases the concentrations of some macro- and micronutrients in plant tissues (Iyer and Scott, 2001; Jala and Goyal, 2006; Shaheen et al., 2014; Singh et al., 2010; Yunusa et al., 2012).

Selenium (Se) is an essential micronutrient for both humans and animals. Low dietary intakes of Se may cause a number of diseases such as cardiovascular diseases, hypothyroidism, reduced male fertility, declined cognition, weakened immune system, and enhanced susceptibility to infections and cancer (Quang Toan et al., 2018; Rayman, 2012; Schrauzer and Surai, 2009). More than a billion people around the world are estimated to suffer from Se deficiency (Combs, 2001). Since plants are the main source of dietary Se for humans and livestock, and Se concentration in edible plants is determined by the phytoavailability of Se in soils, the lack of Se in human diets is mainly due to the production of low-Se crops on soils with low Se content or bioavailability (Broadley et al., 2006; White, 2016; Zhu et al., 2009). Selenium is not an essential element for plants, and Se concentrations in edible plants vary greatly (White, 2016). Agronomic biofortification of food crops with Se using Se-enriched fertilizers is feasible; in theory, it is

an appropriate strategy to increase dietary intake of Se by humans and live-stock, and address the Se deficiency problem effectively (White and Broadley, 2009).

Coal fly ash is often rich in Se, and can result in increased Se concentrations in plant tissues when applied to soils (Gutenmann et al., 1979; He et al., 2017a; Pathan et al., 2003; Patra et al., 2012). Therefore, it is promising to biofortify crops with Se by application of CFA to soils. However, too much Se can cause toxicity to plants, and excessive dietary intake of Se can be harmful to humans and livestock (White, 2016; Zhu et al., 2009). The application rate of CFA should be carefully determined. Furthermore, CFA is an anthropogenic waste material that has a very complex and variable composition (Jala and Goyal, 2006; Shaheen et al., 2014; Zacco et al., 2014). Besides plant nutrients and Se, CFA also contains significant quantities of potentially toxic trace elements (PTEs), including toxic metals such as lead (Pb) (Dar et al., 2017; Love et al., 2013), cadmium (Cd) (Dar et al., 2017; Schneider et al., 2014) and chromium (Cr) (Kingston et al., 2005; Raja et al., 2015), and metalloids such as arsenic (As) (Love et al., 2013; Veselska et al., 2013), and mercury (Hg) (Mukherjee et al., 2008; Silva et al., 2012). Coal fly ash may also contain high levels of organic compounds such as polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) (Li et al., 2014b; Ribeiro et al., 2014; Sahu et al., 2009), and radionuclides such as the U– and Th–series as well as ^{40}K and ^{137}Cs (Lauer et al., 2015; Noli et al., 2017). These may be released into the environment and taken up by food crops, potentially contaminating the food chain and causing problems for human and animal health (Lauer et al., 2015; Ribeiro et al., 2014). The contribution of CFA application to the improvement of soil nutrient supply and crop production should be carefully evaluated; the potential risk of contamination of the food chain warrants careful assessment, and the utilization of CFA for Se biofortification should be judiciously investigated.

In this chapter, we focus on the potential beneficial application of CFA as a soil amendment for Se biofortification. The concentration and speciation of Se in CFA are surveyed and described. Factors affecting Se mobility and bioavailability in CFA–amended soils, and plant uptake of Se from CFA–amended soils are summarized; effects of CFA application on Se accumulation by plants, plant growth and crop yield are assessed. The disadvantages, potential negative effects, and hazards of CFA when applied to soil are listed and discussed, and measures for efficient use of CFA for Se biofortification and hazard reduction and prevention are proposed.

2. Concentration and speciation of selenium in CFA

Concentration and speciation of Se in CFA vary greatly, depending on the type and composition of feed coals, and combustion conditions (Catalano et al., 2012; Huggins et al., 2007; Liu et al., 2013; Luo et al., 2011). According to Page et al. (1979), Se concentration in CFA is in the range of 0.2–134 µg Se g^{-1}. Concentration of Se in CFA derived from bituminous coals is typically in the range of 10–20 µg Se g^{-1}, but it can be as high as 200 µg Se g^{-1} (Jiao et al., 2013). Concentrations of Se in CFAs generated in coal–fired power plants in different regions of the world are listed in Table 1.

Only inorganic Se species are present in CFA (Liu et al., 2013). In CFAs collected from four Australian power stations, Se was mainly present in the form of Se(IV), i.e., selenite, with a minor presence of Se(VI), i.e., selenate, when Se speciation was determined through the first derivative of the XANES spectra (Shah et al., 2007). When analyzing the speciation of Se in 10 CFAs collected from full–scale pulverized coal–fired utility boilers burning a range of coals using X-ray absorption fine structure spectroscopy (XAFS), Huggins et al. (2007) found that Se was predominantly present as selenite species. For all five representative Class C CFAs from combustion of subbituminous Powder River Basin coal, Se also occurred predominantly as Se(IV) (Luo et al., 2011). In one CFA analyzed by Huggins et al. (2007) and one CFA analyzed by Luo et al. (2011), there was a minor amount of Se(0), which was likely associated with the high content of unburned carbon in the samples and less soluble than selenite. However, for CFAs from the TVA-Kingston fossil plant, results of XANES showed that Se was mainly present as elemental Se (>57%), followed by selenite (11–42%) and selenate (<5%) (Liu et al., 2013). The differences between the results of Liu et al. (2013) and other studies (Huggins et al., 2007; Luo et al., 2011; Shah et al., 2007) are likely caused by the variation in the CFA treatments in the combustion systems, e.g., the injection of activated carbon upstream for Hg control (Liu et al., 2013). The presence and relative proportion of selenite and selenate should be interpreted with care, because the change of Se oxidation state induced by synchrotron radiation. Based on the systematic changes observed in consecutive XANES spectra of Se in CFAs collected from a power plant burning subbituminous coal in Alberta, Canada, it has been estimated that about 15–20% selenite can be oxidized to selenate after exposing the CFA to the synchrotron beam for 2 h (Huggins and Sanei, 2011).

Table 1 Concentrations of selenium (Se) in coal fly ashes (CFAs) generated in coal-fired power plants in different regions of the world.

Country	Location of power plant	Type of feed coal	Se concentration in the CFA ($\mu g\,g^{-1}$)	Reference(s)
Australia	Unspecified	Unspecified	1.1–5.2 (acid-generating CFA), 2.3–3.7 (alkali-generating CFA)	Yunusa et al. (2006)
Bulgaria		Bituminous coal	13.8 (1.4–32.2)	Silva et al. (2012)
China	Anhui	Pulverized Permian coals from the Huainan coalfield	2.8 (2.1–3.2)	Li et al. (2014b)
	Xinjiang	Jurassic subbituminous coals	3.3 (2–5)	Li et al. (2014)
	Jungar thermal power plant, Inner Mongolia	Permian coals from the Hedaigou coalfield	11.5	He et al. (2017a)
European countries including Spain, Netherlands, Greece, Italy	23 different power plants	High-Ca lignite, subbituminous coal, bituminous and anthracitic coals	3–30	Moreno et al. (2005)
India	Unspecified	Unspecified	0.6–2.6	Ram and Masto (2010)
Mexico	Coahuila	Mexican mineral coal	6	Medina et al. (2010)
Poland	Unspecified	Bituminous coals	4.0 (1.5–7.6)	Franus et al. (2015)
		Lignite	4.5 (0.8–10.5)	

The United States	21 different states	Various type of coals	8.0 (1.2–16.5)	Gutenmann et al. (1976)
	Lansing, New York	Unspecified	13.3 in 1986, 10.1 in 1996	Gutenmann et al. (1998)
	Unspecified	Low-S bituminous coals	26.8 (22−31)	Huggins et al. (2007)
	Unspecified	Pennsylvania and West Virginia Bituminous coals	10	
	Southeastern U.S.	Eastern U.S. bituminous coals	14.9 (7.7–23.1)	Bhattacharyya et al. (2009)
		Powder River Basin coal	11.6	
	Kingston Fossil Plant in Tennessee	Unspecified	6	Liu et al. (2013)
	Michigan and North Carolina	Unspecified	10.4 and 28.9	Chen and Li (2006)
	Unspecified	Subbituminous Powder River Basin coal	12.1 (7.4–15.0)	Luo et al. (2011)
	Brandon's horse, Paul Smith Precipitator, Morgan Town power plants in Maryland	Unspecified	35.3 (21.4–46)	Cetin and Aydilek (2013)
	Columbia	Unspecified	24	

Results of leaching experiments have confirmed that the dominant chemical forms of Se in CFAs are extractable species. About 0.9–10% and 8–13% Se was removed from some Australian acidic CFAs and alkaline CFAs by leaching solutions, which were made by adjusting ultra-pure Milli-Q water to different pH values using HCl and NaOH (Jankowski et al., 2006). For CFAs obtained from six coal-fired power plants in various countries, the results of sequential leaching and Inductively Coupled Plasma Mass Spectrometry (ICP–MS) analysis showed that most of the Se occurs as exchangeable and water-soluble species, which account for 6.7–42.0% (21.8% on average) of the total Se; very little Se bound to carbonates and Fe-Mn oxides was detected, and only one out of the six CFAs showed the presence of Se bound to organic matter which accounted for 39.0% of the total Se; the residual fraction of Se bound to SiO_2 was 45.5–93.3% (71.7% on average) of the total Se. The speciation results of water-soluble Se obtained by a high performance liquid chromatography equipped with an ODS-3 column and ICP–MS (HPLC–ICP–MS) showed that Se(IV) is the dominant species, and the ratio of Se(VI) to Se(IV) was higher in acidic CFAs than in alkaline CFAs (Narukawa et al., 2005). Medina et al. (2010) and Neupane and Donahoe (2013) also found that Se mostly occurs in the form of oxyanions such as selenite in CFA leachates under alkaline conditions. In the leachates of some TVA ashes, selenite is the major dissolved species of Se and accounts for 75–94% of the total Se (Liu et al., 2013). For a CFA obtained from the Jungar thermal power plant burning Permian coals from the Hedaigou coalfield in Inner Mongolia, China, total Se concentration determined using ICP–MS after an aqua regia digestion and a multi-acid (HNO_3–$HClO_4$–HF) digestion is 11.5 (He et al., 2017a) and 16.0 µg Se g^{-1} (He, H., unpublished work), respectively, while the sum of water-soluble, exchangeable and carbonates-bound Se is 9.5 µg Se g^{-1} (He et al., 2017a), and organic matter-bound Se is 2.2 µg Se g^{-1}, but very little Se bound to Fe-Mn oxides was detected (He H, unpublished work).

3. Factors affecting the mobility and bioavailability, and plant uptake of selenium

The mobility and bioavailability of Se in the environment mainly depends on the valence states of Se, with the oxidized forms of Se such as selenite and selenate being highly soluble and more mobile when compared with less soluble forms such as elemental Se (Liu et al., 2013). As selenite adsorbs more strongly and over a greater pH range than selenate,

the predominant occurrence of selenite in most CFAs indicates that once Se is released from CFAs, its migration in the environment will be strongly affected by adsorption (Luo et al., 2011; Wang et al., 2009). The type of CFA also has a significant impact on the leaching of Se. Adsorption/desorption is one of the major control mechanisms for Se leaching from bituminous CFAs. The leaching amount and rate of Se from bituminous CFAs are both greater than those from sub-bituminous CFAs, possibly due to the large content of Ca in sub-bituminous CFAs, as Ca can form hydration or precipitation products as a sink for Se, thus reducing Se leaching from sub-bituminous CFAs (Wang et al., 2007, 2009). The results of sequential leaching of three CFAs from three full-scale Indian power plants and five CFAs from five U.S. power plants suggests that the solid phase speciation of Se has a more significant effect on the leachability of Se than the total Se concentration does, as a greater proportion of Se is leached from the Ca-rich CFAs than from the Si-rich CFAs, although the Si-rich CFAs have higher Se concentrations than the Ca-rich CFAs (Lokeshappa et al., 2014). As the mobility and bioavailability of inorganic Se increase with decreasing content of iron oxides and hydroxides in the soil (Peak and Sparks, 2002), the content of iron oxides and hydroxides in CFA can also affect the mobility and bioavailability of Se.

In the environment, the mobility and bioavailability of inorganic Se increase with increasing pH (Winkel et al., 2015). For some Australian acidic CFAs, Se concentration in the leaching solution increases with increasing initial pH of the solution; however, for alkaline CFAs, Se concentrations in leaching solutions at different pH are similar, suggesting that Se is present in oxyanions that are highly soluble in alkaline solutions (Jankowski et al., 2006). A few studies have shown that Se from CFAs remains in its anionic forms such as SeO_4^{2-} and SeO_3^{2-} at alkaline pH (Izquierdo et al., 2011; Morar Doina et al., 2012). Leaching experiments performed on spilled TVA ash under a wide range of pH conditions show that the Se concentration in leachates is maximal under extreme acidic (pH 0.4–1.7) conditions, then reaches a minimum value at pH 4.5–7.0, and increases again at pH 12. At near-neutral pH, the predominant Se species might be $HSeO_3^-$, which has a strong sorption affinity for both hydrous ferric oxides and clay minerals, thus resulting in lower Se concentrations in the leachates (Ruhl et al., 2010). For two bituminous CFAs, Se leaching decreases with increasing pH within a very acidic pH range (pH < 3), then reaches minimal levels within the intermediate pH range of 3–8, and increases with increasing pH within the alkaline pH range (pH > 8), due to ash dissolution under extremely

acidic conditions, changes in surface site speciation and Se speciation as a function of pH, and the different adsorption strengths of different Se speciations on surface sites (Su and Wang, 2011). For some U.S. CFAs, the amount of leachable Se increases with an increase of pH from 3 to 13. At the natural pH (7.6–9.5) of these CFAs, the leachable Se comprises Se oxyanions, with selenite being the dominant form. However, at pH 12, both desorption of Se oxyanions and oxidative dissolution of elemental Se seem to contribute to the release of Se from CFAs (Liu et al., 2013). The effects of pH on Se leaching depend on the type of CFAs. For some bituminous CFAs, minimum Se leaching occurs at pH 3–4, while the maximum Se leaching occurs at pH 12, suggesting that selenite is strongly adsorbed by bituminous CFAs under acidic pH conditions and is mostly removed across the entire pH range. However, there is no such trend for sub-bituminous CFAs, from which the release of Se is very low for a pH range between 2 and 12 (Wang et al., 2007). Low soil pH favors the fixation of selenite to the clay minerals, while high pH favors the oxidation of selenite to the far more easily extractable selenates (Tayfur et al., 2010). Therefore, pH is a key factor affecting the mobility and bioavailability of Se in CFA-treated soils.

The distribution of Se species is sensitive to subtle alterations such as redox potential and the presence of redox catalysts. In general, Se solubility and mobility increase with increasing redox potential (i.e., more oxidizing conditions) (Fernandez-Martinez and Charlet, 2009). A number of studies have demonstrated that the magnitude of Se mobilization increases if CFAs are subjected to alkaline conditions, and selenite that is leached from CFAs can be oxidized under oxidizing conditions to selenate, which is less prone to adsorption, but the transformation of selenite to selenate is rather slow (Liu et al., 2013; Ruhl et al., 2010). Other factors such as surface charge, concentrations of other anions and cations on the surface of CFAs can also affect the leaching of Se oxyanions (Su and Wang, 2011). The presence of microbes can affect the Se redox cycling (Sarathchandra and Watkinson, 1981), thus affecting the leaching of Se from CFAs.

The distribution of Se species in CFAs is different from that in soils. In alkaline and well-oxidized soils (pe + pH > 15), Se occurs predominantly as selenate, whereas in well-drained mineral soils with pH from acidic to neutral (7.5 < pe + pH < 15), selenite is the predominant form of Se. In strongly reduced soils (pe + pH < 7.5), selenide becomes the dominant form of Se (Elrashidi, 1987). Studies on the transformation of Se after applying CFAs to different types of soils are lacking.

Soil Se is mainly present in inorganic forms, but it can also be present in organic forms, e.g., as complexes with organic matter and incorporated into organic or organo-mineral colloids (Fernandez-Martinez and Charlet, 2009; Winkel et al., 2015). Soil organic matter (OM) may influence the retention of Se in soils in three ways: (i) facilitating direct complexation with Se by increasing sorption sites (Bruggeman et al., 2007; Dhillon et al., 2007); (ii) indirect complexation via OM-metal complexes (Coppin et al., 2009; Shand et al., 2012); and (iii) microbial reduction and incorporation of Se into amino acids, proteins, and natural organic matter (Abrams et al., 1990; Coppin et al., 2009). Therefore, the organic matter content in both CFA and soil can affect the mobility and bioavailability of Se in CFA-treated soils.

All the above-mentioned factors affecting Se mobility and bioavailability can also affect the uptake of Se by plants, and Se species is one of the most important factors affecting Se uptake by plants, with selenate being highly bioavailable whereas selenite is less available to plants. The effects of pH on plant Se uptake mainly depend on soil type. Uptake of Se increases with increasing pH in sandy and loamy soils but not in clay soils (Chilimba et al., 2011; Gissel-Nielsen, 1971; Johnsson, 1991), possibly because clay soils retain more Se than sandy and loamy soils, but Se retained by clay soils is less available for plants (Tayfur et al., 2010); while Se uptake decreases with increasing pH in soils rich in organic matter (Johnsson, 1991). As organic matter increases Se retention in the soil, we expect Se uptake to decrease with increasing organic matter content (De Temmerman et al., 2014; Johnsson, 1991). However, Se uptake increases with increasing organic matter content in soils with moderate organic matter content, but decreases with increasing organic matter content when the soil organic matter content is high (Johnsson, 1991). The variation in the effects of organic matter on Se uptake may be attributed to differential partitioning of Se to fulvic and humic acids, which have a different sorption capacity for Se, and thus affect Se bioavailability in the soil (Qin et al., 2012). Furthermore, increases in soil organic matter content can increase microbial activity, thereby promoting Se uptake by plants (Gustafsson and Johnsson, 1994; Yasin et al., 2015).

Factors such as competing ions, e.g., sulfate, phosphate, and organic acids, and the microbial community and activity in the soil can also affect Se bioavailability and plant Se uptake; the uptake of Se can also vary considerably among plant species (Duran et al., 2013; Hopper and Parker, 1999; Oram et al., 2011; White, 2016; Zhu et al., 2009). There are interactions between selenate and sulfate, and between selenite and phosphate in both soil and plants. Addition of sulfate to soil can significantly increase the

bioavailability of selenate by decreasing selenate sorption; similarly, addition of phosphate to soil can decrease selenite sorption, thus increasing the bio-availability of selenite (Li et al., 2015). However, 2-year field trials carried out by Stroud et al. (2010) to study the response of UK wheat to Se and S fertilization and residual effects of Se showed that S fertilization pro-duced contrasting effects in 2 years. In the first year, when the crop was not deficient in S, S fertilization significantly increased grain Se concentration, whereas in the second year, when S fertilization resulted in significant crop yield response, the grain Se concentration decreased markedly in S-fertilized plots. Addition of sulfate enhanced the recovery of selenate added to soils, possibly due to a suppression of selenate transformation to other unavailable forms in soils. The results of Stroud et al. (2010) suggest that S can enhance Se availability in soil but inhibit selenate uptake by plants, and there are complex interactions between S and Se, in which both soil and plant physiological processes are involved. Selenate is transported across the plasma membrane of root cells by high-affinity sulfate transporters (Cabannes et al., 2011; White et al., 2004), while selenite is thought to be transported by phosphate transporters (Li et al., 2008; Zhang et al., 2014). Sulfate can inhibit selenate uptake through competition and downregulation of the expression of genes encoding sulfate/selenate transporters (Shinmachi et al., 2010), and a similar effect of phosphate inhibiting selenite uptake has been identified (Stroud et al., 2010; Terry et al., 2000; White, 2016; Zhang et al., 2014). Sulfate deprivation increases selenate uptake (Cabannes et al., 2011), and selenite uptake is greatly enhanced under P-starvation conditions (Li et al., 2008; Zhang et al., 2014). Rhizosphere organic acids can also compete with Se for sorption sites, or chelate Se (Saha et al., 2007; Zhou et al., 2007). Furthermore, a few rhizosphere processes can enhance Se bioavailability by oxidizing reduced soil Se to more soluble Se(VI) species (Oram et al., 2011). Inoculation with rhizosphere bacteria and arbuscular mycorrhizal fungi (AMF) enhances Se uptake by plants (de Souza et al., 1999; Duran et al., 2013; Yu et al., 2011).

The partitioning of Se in plants depends on the speciation of Se in soil; selenate absorbed by roots is readily translocated to shoots, with only a small fraction converted to organic species, while selenite absorbed by roots is mainly retained in roots and mostly converted to organic species (Li et al., 2008; Terry et al., 2000; Yu et al., 2011). Uptake and translocation of Se may also be influenced by plant species and genetic traits, as well as the phase of development and physiological conditions of plants (Banuelos et al., 2002; Pickering et al., 2000; Terry et al., 2000). Most plant species are

non–Se-accumulators, which usually contain only 1–10 μg Se g^{-1} dry matter (DM); they are usually intolerant to elevated Se levels in the environment and not able to accumulate >25 μg Se g^{-1} DM. However, Se-accumulators can accumulate high levels of Se, i.e., 1–15 mg Se g^{-1} DM, and are also characterized by extraordinarily high Se to S ratios (Pilon-Smits et al., 2009; Terry et al., 2000; White, 2016; White et al., 2007). Selenium-accumulators and non-accumulators presumably have transporters with contrasting sulfate/selenate selectivities, with the transporters in accumulators being Se-specific, showing a greater affinity for selenate than sulfate, thus enabling preferential uptake of selenate over sulfate (DeTar et al., 2015; El Mehdawi et al., 2015; Stroud et al., 2010; White et al., 2004). Translocation of Se from roots to shoots is very efficient in Se-accumulators, but inefficient in non-accumulators, very likely because the transporters mediating selenate and sulfate uptake and translocation have a higher affinity for selenate than for sulfate (Lindblom et al., 2013; Owusu-Sekyere et al., 2013).

4. Effects of CFA on selenium bioaccumulation by plants

Application of Se-rich CFA to low-Se soils can increase Se uptake by plants; it can also affect plant S uptake and Se/S ratio. The effects of CFA on plant Se accumulation depend not only on the characteristics of the CFA and soil, but also on plant species and varieties, and vary among different plant tissues.

4.1 Effects of CFA on selenium concentration in plants

A number of field studies and pot experiments have demonstrated that the presence of CFA can result in increased Se concentrations in plants (Table 2). For example, when grown in soils containing 10% of the CFA from the Lansing landfill site, beans, cabbage, carrots, millet, onions, potatoes, and tomatoes showed significantly higher Se concentrations (up to 1 μg Se g^{-1} DM) compared with 0.02 μg Se g^{-1} DM in control plants (Gutenmann et al., 1976). For alfalfa, white sweet clover (*Melilotus alba*), red clover (*Trifolium pratense*), timothy (*Phleum pratense*), oat (*Avena sativa*), rutabaga (*Brassica napus*), wild carrot (*Daucus carota*), brome grass (*Bromus inermis*), bird's-foot trefoil (*Lotus corniculatus*), bitterweed (*Picris hierucioides*), crown vetch (*Coroilla varia*), milkweed (*Asclepias syriaca*), Se concentrations were generally significantly higher in plants grown on CFA landfill sites than in those grown on non-landfill sites. Mean concentrations of Se in plants or

Table 2 Effects of CFA application on selenium (Se) concentration in plants.

Type of study	Type of plant sample(s)	Soil type and Se concentration in the soil ($\mu g\,g^{-1}$)	CFA application rate and Se concentration in the CFA ($\mu g\,g^{-1}$)	Se concentration in plants (μg Se g^{-1} DM)	Reference(s)
Field study	Aerial parts of yellow sweet clover (*Melilotus officinalis*)		Gravelly loam subsoil ($Se_{soil}=2.3\,\mu g\,g^{-1}$) at a nonlandfill site	0.07	Furr et al. (1975)
			CFA ($Se_{CFA}=21.3\,\mu g\,g^{-1}$) at a CFA landfill site in Lansing, New York	5.3	
Field study	Aerial parts of white sweet clover (*Melilotus alba*)		CFA ($Se_{CFA}=22.9\,\mu g\,g^{-1}$) at a CFA landfill site in Lansing, New York	14	Gutenmann et al. (1976)
			CFA ($Se_{CFA}=21\,\mu g\,g^{-1}$) at a CFA landfill site in Endwell, New York	69	
Field study	Above-ground tissues (green chop) of three corn (*Zea mays*) cultivars		A nonlandfill site in Ithaca, New York	0.02	Arthur et al. (1992a)
			CFA ($Se_{CFA}=5.07\,\mu g\,g^{-1}$) at a CFA landfill site in Lansing, New York	0.20–0.41	
Field study	Various plant parts of a series of plant species		Nonlandfill sites	0.01–0.14 (0.06 on average)	Arthur et al. (1992b,c)
			A CFA landfill site in Lansing, New York	0.13–7.19 (1.74 on average)	

Field study	Alfalfa (*Medicago sativa*)	Reclaimed land at the Highvale coal mine near Edmonton, Alberta, Canada	$0\,t\,ha^{-1}$	0.03 (first year), 0.46 (second year)	Hammermeister et al. (1998)
			25, 50, 100, 200, and $400\,t\,ha^{-1}$ ($Se_{CFA}=4\,\mu g\,g^{-1}$)	0.09–0.36 (first year), 0.22–0.52 (second year)	
	Brome (*Bromus inermis*) grass	Reclaimed land at the Highvale coal mine near Edmonton, Alberta, Canada	$0\,t\,ha^{-1}$	0.12 (first year), 0.17 (second year)	
			25, 50, 100, 200, and $400\,t\,ha^{-1}$ ($Se_{CFA}=4\,\mu g\,g^{-1}$)	0.10–0.56 (first year), 0.10–0.24 (second year)	
	Barley (*Hordeum vulgare*) silage	Reclaimed land at the Highvale coal mine near Edmonton, Alberta, Canada	$0\,t\,ha^{-1}$	0.19 (first year), 0.00 (second year)	
			25, 50, 100, 200, and $400\,t\,ha^{-1}$ ($Se_{CFA}=4\,\mu g\,g^{-1}$)	0.15–0.43 (first year), 0.00–0.05 (second year)	
Field study	Centipede grass (*Eremochloa ophiuroides*)	Congaree silt loam	$0\,t\,ha^{-1}$	0.13	Adriano et al. (2002)
			$280\,t\,ha^{-1}$ ($Se_{CFA}=8.4$–$11\,\mu g\,g^{-1}$)	1.9 (third year), 1.2 (fourth year)	
			$560\,t\,ha^{-1}$ ($Se_{CFA}=8.4$–$11\,\mu g\,g^{-1}$)	4.3 (third year), 2.3 (fourth year)	
			$1120\,t\,ha^{-1}$ ($Se_{CFA}=8.4$–$11\,\mu g\,g^{-1}$)	6.5 (third year), 4.0 (fourth year)	

Table 2 Effects of CFA application on selenium (Se) concentration in plants.—cont'd

Type of study	Type of plant sample(s)	Soil type and Se concentration in the soil ($\mu g\,g^{-1}$)	CFA application rate and Se concentration in the CFA ($\mu g\,g^{-1}$)	Se concentration in plants (μg Se g^{-1} DM)	Reference(s)
Field study	A grass mixture	Uthordents	$0\,t\,ha^{-1}$	0.13	Punshon et al. (2002)
			280, 560, and $1120\,t\,ha^{-1}$ ($Se_{CFA}=12\text{--}17\,\mu g\,g^{-1}$)	5.38	
Field study	Maize (*Zea mays*) grains	Crop land soil at Malud, Odisha, India ($Se_{soil}=1.2\,\mu g\,g^{-1}$)	$0\,t\,ha^{-1}$	0.16	Patra et al. (2012)
			$200\,t\,ha^{-1}$ ($Se_{CFA}=2.7\,\mu g\,g^{-1}$)	0.23	
		Crop land soil at Dhenkanal, Odisha, India ($Se_{soil}=2.5\,\mu g\,g^{-1}$)	0	0.14	
			$200\,t\,ha^{-1}$ ($Se_{CFA}=2.7\,\mu g\,g^{-1}$)	0.19	
	Rice (*Oryza sativa*) grains	Crop land soil at Malud, Odisha, India ($Se_{soil}=1.2\,\mu g\,g^{-1}$)	0	0.60	
			$200\,t\,ha^{-1}$ ($Se_{CFA}=2.7\,\mu g\,g^{-1}$)	0.79	
		Crop land soil at Dhenkanal, Odisha, India ($Se_{soil}=2.5\,\mu g\,g^{-1}$)	0	0.11	
			$200\,t\,ha^{-1}$ ($Se_{CFA}=2.7\,\mu g\,g^{-1}$)	0.69	
Field study	*Cassia occidentalis* leaf		An uncontaminated reference site (Se not detected)	0.52	Love et al. (2013)
			The substrate of a CFA basin ($Se_{substrate}=0.08$) of Badarpur Thermal Power Station in Delhi, India	1.07	

Field lysimeter experiment	Bermudagrass (*Cynodon dactylon*) leaf	Sandy soil (Karrakatta sand) from Western Australia	0%	0.03	Pathan et al. (2003)
			5%	0.13	
			10%	0.31	
			20%	0.63	
Pot experiment	Cabbage (*Brassica oleracea* var. green winter)	Teel silt loam soil	0%	0.05	Gutenmann et al. (1976)
			10% of each of 15 CFAs containing different concentrations of Se	0.2–3.7	
Pot experiment	Alfalfa	Hapludalf	0%	0.07 (74 days), 0.06 (118 days)	Arthur et al. (1993)
			10%	0.96 (74 days), 1.05 (118 days)	
			20%	2.31 (74 days), 2.34 (118 days)	
Pot experiment	Onion (*Ilium cepa*)	2:1 (v/v) vermiculite: spaghnum peat moss standard plant growth medium	0%	0.038	Gutenmann and Lisk (1996)
			10% ($Se_{CFA} = 13.4\,\mu g\,g^{-1}$)	0.032	
			25% ($Se_{CFA} = 13.4\,\mu g\,g^{-1}$)	0.054	
			50% ($Se_{CFA} = 13.4\,\mu g\,g^{-1}$)	0.138	
Pot experiment	Onion	2:1 (v/v) vermiculite: spaghnum peat moss standard plant growth medium ($Se_{soil} = 0.08\,\mu g\,g^{-1}$)	0%	0.04	Gutenmann et al. (1998)
			7.59% ($Se_{CFA} = 13.3\,\mu g\,g^{-1}$)	0.25	
			10.1% ($Se_{CFA} = 10.1\,\mu g\,g^{-1}$)	0.22	

plant parts on CFA landfill sites fell in the range of 0.13–7.19 (1.74 on average) µg Se g^{-1} DM, being 2–134 (38 on average) times higher than those on non-landfill sites which were 0.01–0.14 (0.06 on average) µg Se g^{-1} DM (Arthur et al., 1992b,c). There are significant differences in Se concentrations among plants of the same species growing on different CFA landfill sites, very likely due to the differences in Se concentrations in the CFA among different landfill sites (Arthur et al., 1992b; Woodbury et al., 1999). Selenium concentration also varies among tissues of plants treated with CFA. For white sweet clover growing voluntarily on two CFA landfill sites, Se concentration in the topmost 15-cm parts of plants containing much less stem material than the rest of the plants is up to five times these concentrations of the entire aerial parts, and is >200 µg g^{-1} at the Endwell site (Gutenmann et al., 1976). Leaves and kernels of corn (*Zea mays*) had higher Se concentrations than other tissues; stalks and cobs had the lowest Se concentrations, suggesting that Se was mobile in the plant (Arthur et al., 1992a).

The effects of CFA on plant Se concentration also depend on the time since the application of CFA to soil. In the first year after a CFA was applied at 25, 50, 100, 200, and 400 t ha^{-1} to reclaimed fields near Edmonton, Alberta, Canada, alfalfa plants in plots amended with ≥100 t CFA ha^{-1} had significantly higher Se concentrations than those in the control plot in the first year. However, there was no siginificant difference in Se concentration in alfalfa among treatments in the second year. A similar trend was observed for brome grass, of which Se concentration in ≥100 t CFA ha^{-1} treatment (0.34–0.56 µg Se g^{-1} DM) was considerably higher than that in the control (0.12 µg Se g^{-1} DM) in the first year after CFA application, but the differences among treatments were not significant in the second year. There was no significant difference in Se concentration in barley (*Hordeum vulgare*) silage among treatments in either the first or second year after CFA application. The mean Se concentration in alfalfa grown in CFA-amended plots was higher in the second year (0.36 µg Se g^{-1} DM) than that in the first year (0.24 µg Se g^{-1} DM). However, for both brome grass and barley silage, mean Se concentration in CFA-amended plots was higher in the first year (0.33 µg g^{-1} for brome grass, and 0.29 µg Se g^{-1} DM for barley silage) than in the second year (0.17 µg Se g^{-1} DM for brome grass, and 0.01 µg Se g^{-1} DM for barley silage) (Hammermeister et al., 1998). For centipedegrass (*Eremochloa ophiuroides*) growing in a Congaree silt loam treated with different rates of CFA containing 8.4–11 µg Se g^{-1} total Se from a power station of the South Carolina Electric and Gas Co. in Beech Island, SC, U.S., the Se concentration was lower in the fourth year than in the third year since CFA application, indicating that the Se concentration in plants diminishes

with time after a one-off CFA application (Adriano et al., 2002). Application of CFA at high rates significantly increases the Se concentration in plant tissues of a grass mixture by almost 40 times, but the Se concentration in plant tissues drops steadily over time (Punshon et al., 2002).

In a 2-year pot experiment, the shoot Se concentration in four different cuts of alfalfa increased from 0.30–0.50 (0.38 on average) μg Se g^{-1} DM in the control of a loessial soil without CFA to 1.57–3.57 (2.58 on average), 3.33–5.20 (4.57 on average), 5.73–11.70 (8.83 on average), and 8.70–13.97 (11.26 on average) μg Se g^{-1} DM in the 5%, 10%, 20%, and 40% CFA treatment, respectively, representing a 2.9–45.6 times increase (He et al., 2017a, Fig. 1A). When erect milkvetch (Astragalus adsurgens) is harvested 90 (H1) and 150 days (H2) after sowing, the shoot Se concentration in the control of a loessial soil without CFA is 0.35 and 0.33 μg Se g^{-1} DM, but increases to 1.66 and 1.43, 2.83 and 2.67, 6.33 and 5.20, 12.80 and 17.83 μg Se g^{-1} DM in the 5%, 10%, 20%, and 40% CFA treatment, respectively, showing a 3.3–52.5 times increase (Fig. 1D). Unlike the results of the studies cited in the previous paragraph, the Se concentration in alfalfa and erect milkvetch studied by He et al. (2017a) (Fig. 1A and D) did not decline over time; instead, shoots of alfalfa harvested in the second year had higher Se concentrations on average than those harvested in the first year. In the second year of a 2-year pot experiment, the mean leaf Se concentration in two different cuts of alfalfa increased markedly from 1.06 μg Se g^{-1} DM in the control of an eolian sandy soil without CFA to 15.48, 17.13, and 13.90 μg Se g^{-1} DM in the 10%, 20%, and 40% CFA treatment, respectively (Fig. 2A). Mean stem concentration in the control was 0.90 μg Se g^{-1} DM, but rose to 8.38, 9.57, and 7.82 μg Se g^{-1} DM in the 10%, 20%, and 40% CFA treatment, respectively (Fig. 2D). Concentrations of Se in leaves were always higher than those in stems, with mean leaf Se concentration of different cuts 18%, 85%, 79%, and 78% higher than mean stem Se concentration (Fig. 2A and D), similar to the results of Gutenmann et al. (1976), which showed that plant parts containing less stem material had higher Se concentrations than those containing more stem material. Although adding CFA to soil can significantly increase the Se concentration in plant tissues, Se concentrations in plants grown on CFA-treated soil hardly reach the hyperaccumulation level (Terry et al., 2000; White, 2016).

4.2 Effects of CFA on sulfur concentration in plants

Although S and Se are chemically similar, and the S concentration is also often higher in CFAs than in soils (He et al., 2017a; Jala and Goyal, 2006; Khan and Khan, 1996; Masto et al., 2013; Ram et al., 2006, 2007;
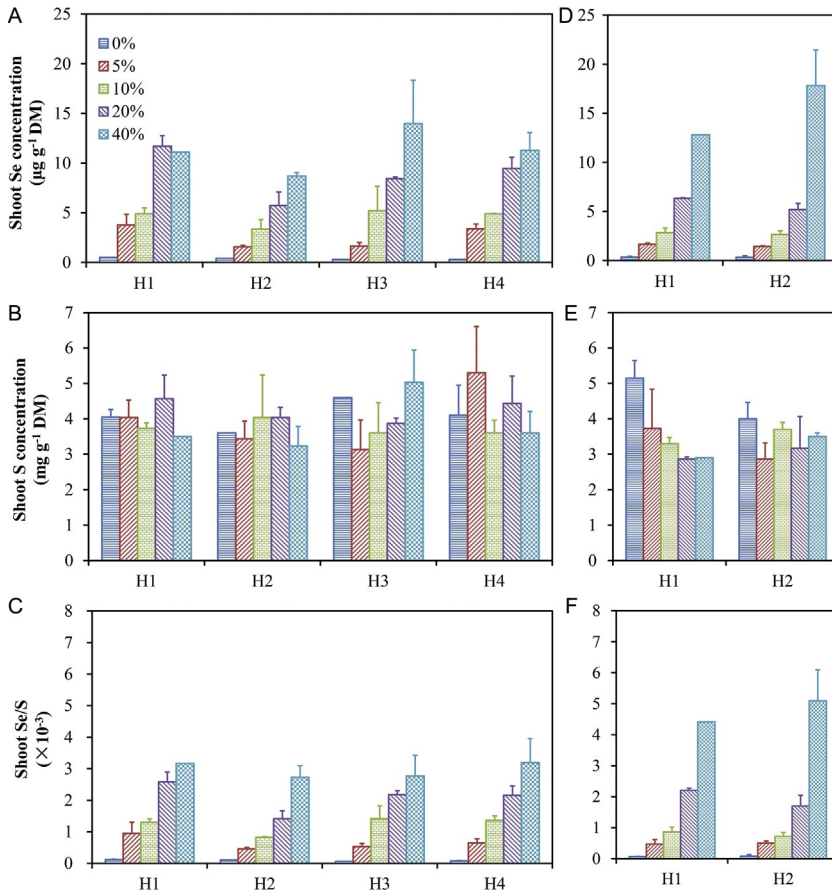
Fig. 1 Concentration of selenium (Se) and sulfur (S), and Se/S ratio in shoots of alfalfa (*Medicago sativa*) and erect milkvetch (*Astragalus adsurgens*) grown in a loessial soil amended with different rates of coal fly ash. Panels (A–C) are for shoots of alfalfa at four consecutive harvests (H1, H2, H3, and H4) of plants in a 2-year pot experiment. Panels (D–F) are for shoots of erect milkvetch at two consecutive harvests (H1 and H2) of plants in a 1-year pot experiment. All data are presented as means + SD ($n=3$). The details of the experimental design can be found in He et al. (2017a, 2018). *The figure was modified after He, H., Dong, Z., Peng, Q., Wang, X., Fan, C., Zhang, X., 2017a. Impacts of coal fly ash on plant growth and accumulation of essential nutrients and trace elements by alfalfa* (Medicago sativa) *grown in a loessial soil. J. Environ. Manage. 197, 428–439.*

Singh and Siddiqui, 2003; Yunusa et al., 2006), the effects of CFA application on plant S concentration are not the same as those on plant Se concentration. Plants grown in some S-deficient soils, especially acid soils, show increased S concentration in the presence of CFA, due to increased
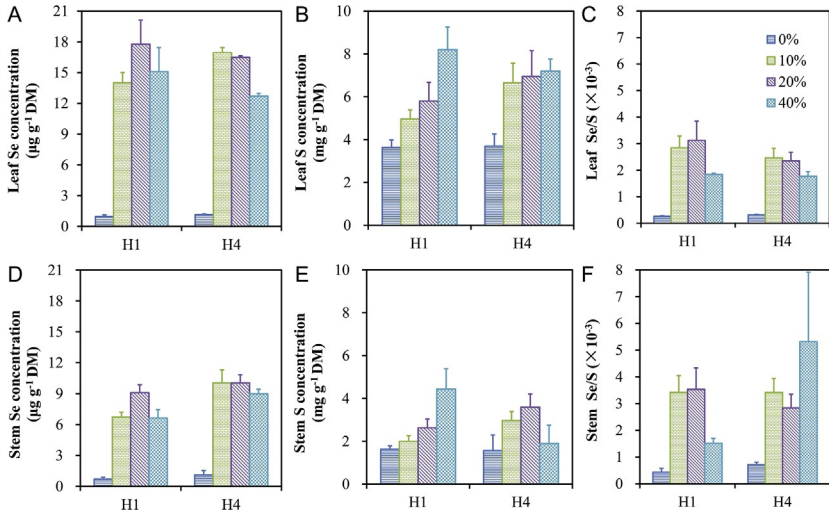
Fig. 2 Concentration of selenium (Se) and sulfur (S), and Se/S ratio in shoots of alfalfa (*Medicago sativa*) at the first (H1) and last (H4) one of four consecutive harvests of plants grown in an eolian sandy soil amended with different rates of coal fly ash in the second year of a 2-year pot experiment. (A) Leaf Se concentration; (B) Leaf S concentration; (C) Leaf Se/S; (D) Stem Se concentration; (E) Stem S concentration; (F) Stem Se/S. Data are presented as means + SD ($n = 3$). The details of the experimental design can be found in He et al. (2018).

concentration of plant-available S in the soil (Adriano et al., 1978; Elseewi et al., 1978). However, the presence of CFA does not always increase the S concentration in plants (Table 3). The leaf S concentration of rutabaga grown on the non-landfill site in Lansing is $9.6\,mg\,S\,g^{-1}$ DM, but drops to $6.6\,mg\,S\,g^{-1}$ DM when grown at the CFA landfill site (Arthur et al., 1992c).

The concentration of S in shoots is not significantly increased when the CFA is added to the loessial soil, but decreases in many cases, especially for erect milkvetch, of which the shoot S concentration declines by 28–44% (38% on average) and 8–28% (17% on average) by CFA treatments when plants are harvested 90 and 150 days after sowing (Fig. 1B and E). However, when the CFA is added to the eolian sandy soil, the S concentrations in both leaves and stems of alfalfa increase considerably, with plants in CFA treatments showing 37–126% (81% on average) higher leaf S concentrations and 22–171% (83% on average) higher stem S concentrations than those in the control, respectively. The leaf S concentration is 85–279% (139% on average) higher than the stem S concentration (Fig. 2B and E). Higher

Table 3 Effects of CFA application on sulfur (S) concentration in plants.

Type of study	Type of plant sample(s)	Soil type	CFA application rate and S concentration in the CFA-treated soil (mg g^{-1})	S concentration in plants (mg S g^{-1} DM)	Reference(s)
Field study	Rutabaga (*Brassica napus*)		A non-landfill site	9.6	Arthur et al. (1992c)
			A CFA landfill site in Lansing, New York	6.6	
Pot experiment	Alfalfa (*Medicago sativa*)	Arizo Calcareous soil	0% (Soluble-S = 0.010)	0.57–0.66	Elseewi et al. (1978)
			8% (Soluble-S = 0.288)	2.3	
		Redding Acid soil	0% (Soluble-S = 0.005)	0.57–0.66	
			8% (Soluble-S = 0.357)	2.2	
	Bermudagrass (*Cynodon dactylon*)	Arizo Calcareous soil	0% (Soluble-S = 0.028)	0.36–0.53	
			8% (Soluble-S = 0.343)	3.2	
		Redding Acid soil	0% (Soluble-S = 0.004)	0.36–0.53	
			8% (Soluble-S = 0.263)	5.2	
Pot experiment	Bush bean (*Phaseolus vulgaris*) seedlings	Troup sandy loam (Grossarenic Paleudults)	0%	1.6	Adriano et al. (1978)
			5% fine CFA	2.9	
			10% fine CFA	4.0	
			20% fine CFA	4.1	
			10% coarse CFA	2.8	
	Corn (*Zea mays*) seedlings	Troup sandy loam (Grossarenic Paleudults)	0%	2.1	
			5% fine CFA	2.2	
			10% fine CFA	2.4	
			20% fine CFA	2.7	
			10% coarse CFA	2.5	

Se and S concentrations in leaves than in stems suggest that after the two elements are taken up by roots, Se is redistributed from older tissues to younger tissues within the plant, in a manner analogous to that for S (White et al., 2004).

4.3 Effects of CFA on selenium to sulfur ratio in plants

The presence of CFA often results in higher Se/S ratios in plant tissues. The mean Se/S in different cuts of alfalfa grown on a CFA landfill site in Lansing, New York was 0.72×10^{-3} (Arthur et al., 1992c), which was higher than that of alfalfa grown in both the loessial soil and eolian sandy soil without CFA, and similar to that of alfalfa grown in the loessial soil amended with 5% CFA. Leaf Se/S is 0.04×10^{-3} for rutabaga grown on the non-landfill site in Lansing, but 0.37×10^{-3} on the CFA landfill site (Arthur et al., 1992c). For both alfalfa and erect milkvetch, shoot Se/S increases significantly with increasing CFA application rate when the CFA is added to the loessial soil (Fig. 1C and F). Shoot Se/S in four different cuts of alfalfa increases from 0.07–0.12 (0.09 on avearge) $\times 10^{-3}$ in the control to 0.46–0.95 (0.65 on avearge), 0.83–1.42 (1.23 on avearge), 1.41–2.59 (2.09 on avearge), and 2.73–3.20 (2.97 on avearge) $\times 10^{-3}$ in the 5%, 10%, 20%, and 40% CFA treatment, respectively, with shoot Se/S in CFA treatments being 3.1–41.6 times higher than that in the control. For erect milkvetch, mean Se/S in shoots harvested 90 and 150 days after sowing rose from 0.08×10^{-3} in the control to 0.49, 0.79, 1.96, and 4.75×10^{-3} in the 5%, 10%, 20%, and 40% CFA treatment, respectively, representing a 5.1–58.4 times increase. When the CFA is added to the eolian sandy soil, both leaf and stem Se/S of alfalfa markedly increases (Fig. 2C and F). Mean leaf Se/S of different cuts in the control is 0.29×10^{-3}, but increases to 2.66, 2.74, and 1.80 x 10^{-3} in the 10%, 20%, and 40% CFA treatment, showing a 8.2, 8.4, and 5.2 times increase, respectively. Mean stem Se/S of different cuts in the control is 0.58×10^{-3}; the values of different CFA treatments are similar, ranging between 3.18 and 3.42×10^{-3}, and 3.34×10^{-3} on avearge. Mean leaf Se/S is 50%, 22%, 14%, and 47% lower than stem Se/S in the control, 10%, 20%, and 40% CFA treatment, respectively.

The Se/S ratio in plant organs may partly depends on the Se/S ratio in the growth substrate, and such dependence is complex (White et al., 2004). The presence of CFA often results in a disproportional increase of S and Se concentration in plant tissues, with Se increasing more markedly than S in most cases. One of the reasons for the disproportional increase of S and Se is

that, when applied to soils, CFA can increase the concentration of plant–available Se in the soil more significantly than that of S. Another possible reason is that, although Se and S are chemically similar and selenate is often thought to enter root cells through sulfate transporters in the plasma membrane of root cells, there may be multiple transport pathways with contrasting sulfate/selenate selectivities (White, 2016; Zhu et al., 2009). Furthermore, the predominant speciation of Se in most CFAs is selenite, which is taken up by plants via a phosphate transporter and does not interact with S like selenate during the uptake process (White, 2016; Zhang et al., 2014; Zhu et al., 2009). The Se/S ratio in plant tissues also depends on plant species, with Se-accumulators having significantly higher Se/S ratios than non–accumulators. For example, the mean leaf Se/S ratio of 37 non-Se-accumulators was 1.72×10^{-3}, but that of a Se-accumulator, *Astragalus racemosus*, reached 14.14×10^{-3} (White et al., 2007).

5. Effects of CFA on plant growth and crop yield

Lower CFA application rates enhance plant growth, but higher CFA application rates inhibit plant growth. When a CFA is added to a normal field soil, plant growth and yield of tomato (*Solanum lycopersicum*) are generally enhanced, with the 40–80% CFA treatment increasing plant growth and yield the most; plant growth and yield are optimal at a 50% or 60% CFA-application rate, from 60% or 70% onward, application of CFA has a deleterious effect (Khan and Khan, 1996). Plant growth of faba bean (*Vicia faba*) is significantly stimulated, and biomass accumulation increases by 27% when a CFA is mixed with sandy loam soils at a 10% application rate; however, plant growth is inhibited and dry matter production declines by 27% at a 30% CFA application rate, although there are no metal toxicity or mineral deficiency symptoms (Singh et al., 1997). Application of 20% and 40% of an Indian CFA to a loam soil causes a significant increase in plant growth and yield of three cultivars of rice, with the 40% CFA treatment increasing plant growth and yield more than the 20% CFA treatment did, while the 60%, 80%, and 100% CFA treatments all have an adverse effect on plant growth and yield (Singh and Siddiqui, 2003). Similar results were reported by Dwivedi et al. (2007), who found that a 10–25% CFA treatment enhances plant growth of three rice cultivars, but higher (≥50%) CFA application rates cause toxicity to plants, as evidenced by the reduction in growth parameters such as plant height, root biomass, number of tillers, grain and straw weight. Plant biomass of *Sesbania cannabina* increases significantly up

to 25% CFA treatment as compared with untreated garden soil, and declines from 25% onward (Sinha and Gupta, 2005). In a field study, the yield of onion (*Allium cepa*) increases with increasing CFA application rate up to $50\,t\,ha^{-1}$, above which the yield decreases (Parab et al., 2015).

For alfalfa and erect milkvetch grown in a loessial soil amended with different rates of CFA, plant growth is always considerably enhanced when the CFA application rate is ≤20%. In most cases, plant growth is also markedly enhanced by the 40% CFA treatment (He et al., 2017a, 2018). However, when CFA application rate reaches 80%, shoot dry mass of alfalfa and erect milkvetch declines by 92% and 86%, respectively (Fig. 3). For alfalfa and erect milkvetch grown in a loessial soil and an eolian sandy soil, an CFA application rate ≥40% does not benefit plant growth, at least not more than lower rates do (He et al., 2017a, 2018).

The effects of CFA on plant growth and yield may depend not only on the type of CFA and soil, but also vary among plant species and cultivars, and may differ with time after application of CFA to soil (Cline et al., 2000; Dwivedi et al., 2007; He et al., 2017a, 2018; Matsi and Keramidas, 1999). Enhanced plant growth and increased yield of crops at lower CFA
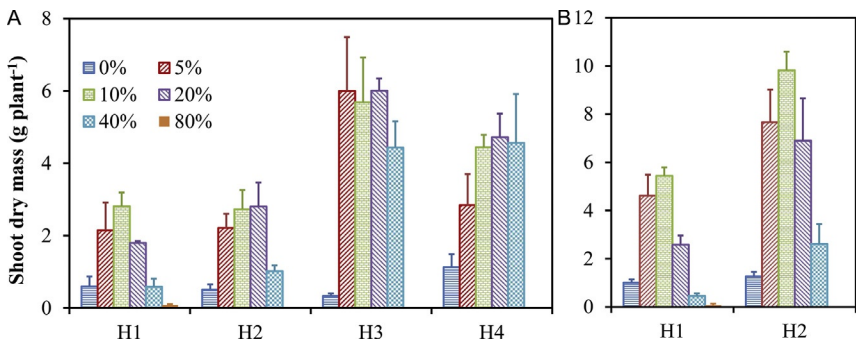

Fig. 3 Shoot dry mass of alfalfa (*Medicago sativa*) and erect milkvetch (*Astragalus adsurgens*) grown in a loessial soil amended with different rates of coal fly ash. Panel (A) is for shoots of alfalfa at four consecutive harvests (H1, H2, H3, and H4) in a 2-year pot experiment. Panel (B) is for shoots of erect milkvetch at two consecutive harvests (H1 and H2) of plants in a 1-year pot experiment. All data are presented as means +SD (*n*=3). *The figure was modified after He, H., Dong, Z., Peng, Q., Wang, X., Fan, C., Zhang, X., 2017a. Impacts of coal fly ash on plant growth and accumulation of essential nutrients and trace elements by alfalfa (*Medicago sativa*) grown in a loessial soil. J. Environ. Manage. 197, 428–439; He, H., Dong, Z., Pang, J., Wu, G.L., Zheng, J., Zhang, X., 2018. Phytoextraction of rhenium by lucerne (*Medicago sativa*) and erect milkvetch (*Astragalus adsurgens*) from alkaline soils amended with coal fly ash. Sci. Total Environ. 630, 570–577, in which the details of the experimental design can be found.*

application rates are related to the beneficial effects caused by improved soil physicochemical properties such as soil texture, water-holding capacity, pH, and supply of plant-essential elements, including P, S, Ca, Mg, as well as improved biological properties of the resultant soil. Inhibited plant growth at higher CFA application rates are very likely the results of the adverse effects caused by high pH and salinity, and enrichment of PTEs such as Mo, B, Se, Pb, Cd, Cr, As, and Hg, and possible deficiency of essential plant nutrients such as nitrogen (N), Cu, and Zn (He et al., 2017a; Pandey and Singh, 2010; Shaheen et al., 2014; Yao et al., 2015). All the above-mentioned factors should be taken into consideration to work out reasonable CFA–application rates.

The application of inorganic Se-fertilizers such as sodium selenate and sodium selenite is an inexpensive and practical method to produce crops containing concentrations of Se high enough to provide likely health benefits to consumers (Broadley et al., 2006; Lyons, 2010; White and Broadley, 2009; Zhu et al., 2009). However, when considering Se biofortification, the use of CFA may have an advantage over the application of inorganic Se-fertilizers in enhancing plant growth. Application of P to an eolian sandy soil and a loessial soil significantly enhanced alfalfa growth, but adding Se at 0.5 and 1 μg Se g^{-1} to the eolian sandy soil and loessial soil in the form of sodium selenate considerably inhibited plant growth and offset the effect of P application; shoot dry mass decreased with increasing selenate application rate, and application of 2 and 4 μg Se g^{-1} soil in the form of sodium selenate even caused lethal damage to plants; adding Se to the soil in the form of sodium selenite does not affect alfalfa growth markedly, regardless of P supply level (He et al., unpublished work). Most Se in CFA-treated soils is likely present in less toxic forms such as selenite, rather than selenate (Liu et al., 2013; Medina et al., 2010; Narukawa et al., 2005; Neupane and Donahoe, 2013); therefore, application of CFA to the soil at appropriate rates does not inhibit plant growth as much as selenate does.

6. Disadvantages, potential negative effects and hazards of CFA application to agricultural land

Despite the significant positive effects of CFA on soil physicochemical properties, plant growth and crop yield, and Se concentration in plants, excess application of CFA to soils likely offsets these positive effects, and there are obvious disadvantages associated with the application of CFA to agricultural land. Adding CFA to the soil may have a series of negative

impacts on the environment and plants, including causing soil salinity, contamination of the soil and water, and the food chain with toxic substances such as high levels of B, Mo, and Se, toxic metals and metalloids, and organic pollutants, macro- and micronutrient deficiency in plants, increased radioactivity and S toxicity, and inhibited microbial activity (Blissett and Rowson, 2012; Haynes, 2009; Pandey and Singh, 2010; Ram and Masto, 2014; Shaheen et al., 2014; Yao et al., 2015). Such negative impacts, or hazards, are constraints to the use of CFA for Se biofortification, and warrant careful and integrative evaluation.

6.1 Salinity

Concentrations of soluble salts such as sulfate, chloride, carbonate, and bicarbonate can be high in unweathered CFA, and salinity is often a major limitation to plant growth in soils amended with unweathered CFA, especially at high doses (Adriano et al., 1980; Gajić et al., 2016; Haynes, 2009; Pandey et al., 2009a; Ram and Masto, 2014). Following the application of two different alkaline CFAs with an electrical conductivity (EC) of 2.7 and 2.5 dS m^{-1} to two Red Mediterranean acid soils with an EC of 0.5 dS m^{-1} at rates equal to 5, 20, and 50 g CFA kg^{-1} soil, soil EC increased considerably, and reached 2.5 dS m^{-1} at the highest CFA application rate (Matsi and Keramidas, 1999). Roy and Joy (2011) reported persistent and dose-dependent increases in EC of CFA-amended red laterite sandy loam soil. When a CFA with an EC of 3.17 dS m^{-1} was added to a loessial soil with an EC of 0.17 dS m^{-1} at 5% and 40%, the EC of the resultant soil was 0.38 and 1.64 dS m^{-1}, respectively, but the EC of the resultant soil decreased with time (He et al., 2017a). Adriano et al. (2002) found that soil salinity increased with increasing CFA application rate in the field; the greatest increases occurred in the initial year of application, but most of the soluble salts were leached from the CFA-treated soil profile into deeper soil layers by the second year, and these salts completely disappeared from the CFA-treated soil profile by the fourth year (Adriano et al., 2002). Weathering of CFA can substantially reduce the concentrations of soluble salts, as they are progressively leached away during the weathering process (Adriano et al., 1980; Haynes, 2009; Ram and Masto, 2014). Due to the porous nature of ash particles, the time required to leach soluble salts away may be long, as the initial leachings only remove salts from the outer surfaces of ash particles (Kukier and Sumner, 1996). However, after sufficient time of weathering, salinity is unlikely a limitation to plant growth when weathered CFA is used

for soil amendment (Haynes, 2009). Therefore, toxicity caused by salinity can be negligible when CFA, especially weathered CFA, is applied to soils at low and moderate rates (Yunusa et al., 2008).

6.2 Boron toxicity

Most unweathered CFAs contain a considerable amount of soluble B and one issue of the most concern for plants grown on soils amended with CFA is B toxicity, which can cause severe plant growth depressions, and B is often considered the principal plant growth inhibitor in unweathered CFA (Adriano et al., 1978; Haynes, 2009; Jala and Goyal, 2006). The concentration of water-soluble B in CFAs is often within the range of $20–60\,\mu g\,g^{-1}$, and can exceed $250\,\mu g\,g^{-1}$ (Adriano et al., 1980; Carlson and Adriano, 1993; Mulford and Martens, 1971). An increase in B concentration in plants grown in substrates containing CFA has been reported in many cases (Gutenmann et al., 1979; Woodbury et al., 1999). Incorporation of a small amount of CFA into soil can help correct B deficiency in some plants such as alfalfa (Mulford and Martens, 1971). However, a $>30\,\mu g\,g^{-1}$ extractable B in soil is considered highly toxic to plants, and plant tolerance to CFA directly parallels their tolerance to B in many cases (Bradshaw and Chadwick, 1980). Characteristic visual B-toxicity symptoms such as leaf necrosis and scorching of the leaf margins are often observed on plants grown on CFA landfills or stockpiles, or on soils amended with CFA at high rates (Adriano et al., 1978; He et al., 2017a). The effects of CFA application on B concentration vary among tissues, for example, CFA application does not affect B concentration in stems of canola (*Brassica napus*), but increases B concentration in leaves (Yunusa et al., 2008).

Boron toxicity can be far more damaging if acidic unweathered CFA is incorporated into acidic soils, as B availability increases with decreasing soil pH (Adriano et al., 1978). However, incorporation of CFA into acidic clay and sandy soils in Southern Ontario showed no significant effect on hot-water extractable B in the soil, possibly due to the increase in soil pH, and application of CFA to the soils at $5–50\,t\,ha^{-1}$ in the field did not result in accumulation of B in plants in quantities that would be of concern for plant or human health and meat consumption (Cline et al., 2000). When an alkaline CFA (pH $= 10.1$) was applied to an acidic soil (pH $= 5.8$) at $40–120\,t\,ha^{-1}$, both hot-water extractable B in the soil and B concentration in rice leaves was increased, but did not exceed toxic levels, and most B contributed by CFA application was present in the residual form,

which is not plant–available (Lee et al., 2008). Plants of red fescue (*Festuca rubra*) grown on CFA deposits where the CFA had higher total and available B concentrations than the soil at the control site showed higher leaf B concentrations than those grown on the soil at the control site, and reached a toxic level (Gajić et al., 2016).

Because B is a relatively mobile element, the water-soluble B concentration in CFA normally decreases with time as weathering and leaching occur, but such a process is often slow and may well take a couple of years before toxic effects of B can decline to tolerable levels (Adriano et al., 1978; Gajić et al., 2016; Haynes, 2009). Concentrations of B in centipedegrass increased with increasing CFA application rate in the field, and B concentrations in plant tissues decreased with time, but such decrease did not parallel the decrease in B concentration in the top soil within the rooting zone (Adriano et al., 2002). In a 2-year pot experiment, applying a CFA to a loessial soil markedly increased B concentration in alfalfa shoots (Fig. 4A), with shoot B concentration increasing the most pronounced, i.e., by 3.7–12.4 times, by CFA treatments in the first harvest, in which shoot B concentrations in all CFA treatments were higher than those in
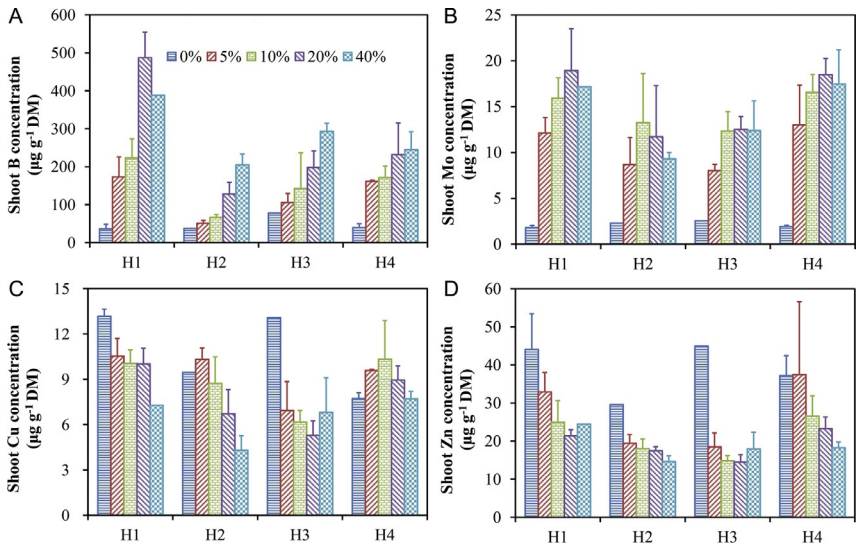

Fig. 4 Concentration of boron (B) (A), molybdenum (Mo) (B), copper (Cu) (C), and zinc (Zn) (D) in shoots at four consecutive harvests (H1, H2, H3, and H4) of alfalfa (*Medicago sativa*) grown in a loessial soil amended with different rates of coal fly ash in a 2-year pot experiment. All data are presented as means + SD ($n = 3$). The details of the experimental design can be found in He et al. (2017a).

later harvests (He et al., 2017a). This suggests that plant–available B concentrations in CFA-amended soils declined with time, and addition of weathered CFA is advisable, rather than applying unweathered CFA (Pandey et al., 2009b).

6.3 Molybdenum toxicity

Most CFAs are rich in Mo, which is highly mobile, especially in alkaline CFAs, and would be leached by rainfall into ground and surface waters, and cause environmental contamination and potential hazards (Haynes, 2009; Jankowski et al., 2006; Tsiridis et al., 2012; Yao et al., 2015). A considerable proportion of Mo in weathered CFA at a 20-year-old CFA dump was associated with the water-soluble and carbonate fraction and significantly leached from the labile phases (Nyale et al., 2014). The total cumulative concentration of Mo in leachates of sub-bituminous CFAs in India obtained by serial batch leaching simulating the rainwater condition exceeded the World Health Organization (WHO) recommended value for drinking water (Praharaj et al., 2002). Concentration of Mo in leachates of a bituminous CFA obtained under acid conditions exceeds the highest Mo concentration recommended in Environment Quality Standard for Surface Water (Wang et al., 2008).

Application of CFA to soil can significantly increase Mo concentrations in plant tissues. For alfalfa, birdsfoot trefoil, brome, orchard grass, and timothy grown on soil amended with $112.5\,t\,CFA\,ha^{-1}$, Mo concentrations in all five successive cuts of all crops were consistently increased, when compared with plants grown on untreated soil (Gutenmann et al., 1979). Concentrations of Mo in plants grown on a soil-capped CFA landfill near Dunkirk, New York were greater than those in the same species harvested concurrently from a non-landfill site (Woodbury et al., 1999). Concentration of Mo in centipedegrass tissues increased with increasing CFA-application rate in the field, and also considerably increased with time, especially at high CFA-application rates (Adriano et al., 2002). In a 2-year pot experiment, shoot Mo concentrations in alfalfa shoots of all cuts were considerably increased, i.e., 2.2–9.5 times, when a CFA was applied to a loessial soil, but there was no obvious trend of change in shoot Mo concentration over time (Fig. 4B), although exchangeable Mo concentrations in the CFA-amended soils increased first, and declined with time (He et al., 2017a). The effects of CFA application on Mo concentrations in plants

are tissue-specific, e.g., Mo concentrations in canola stems were not affected by CFA application, but those in leaves were increased (Yunusa et al., 2008).

Application of CFA may result in accumulation of Mo in plant tissues to toxic levels, and consequently influence human and animal health (Adriano et al., 1980; Basu et al., 2009). The window of safe Mo concentrations for animals is narrow (Adriano et al., 2002); a small amount of Mo is essential in animal nutrition, but continuous consumption of forage with elevated Mo concentrations may induce physiological disorders in livestock animals (Adriano et al., 1980). After consuming plant material grown on CFA-amended soils, elevated levels of Mo were detected in eggs and body tissues of some poultry, and in body tissues of some livestock (Adriano et al., 1980). At high Mo levels, there may be Mo-induced Cu deficiency (molybdenosis) in animals (Adriano and Weber, 2001; Tolle et al., 1983), especially when S levels are also high (Hansen et al., 2008; Sinclair et al., 2013), and Mo toxicity in livestock fed with crops grown on CFA-amended soil has been reported in Great Britain (Tolle et al., 1983).

6.4 Selenium toxicity

Selenium in CFA can easily leach and readily contaminates soil and water, and finally cause contamination of the food chain (Haynes, 2009; Pandey and Singh, 2010). Selenium is not an essential element for vascular plants, but it is essential for humans and animals. However, too much Se in soil and plants is toxic for plants, and there is a narrow window between Se deficiency and toxicity in many organisms, including humans and animals (Pilon-Smits et al., 2009; White, 2016). The recommended Se concentration in the feed is $0.1-1\,\mu g\,Se\,g^{-1}$ feed for proper animal nutrition; $<0.01\,\mu g$ $Se\,g^{-1}$ feed is considered inadequate, while a $>5\,\mu g\,Se\,g^{-1}$ feed can cause Se toxicity in animals and is likely detrimental, if such feed makes up 100% of the animal ration (Tinggi, 2003; Underwood, 1977). Elevated Se concentrations in plants grown on CFA-treated soils are a concern. Although in most cases Se concentrations in plants on CFA-treated soils are not toxic to plants, continuous consumption of forage with elevated Se concentrations may induce physiological disorders and pose a potential hazard to livestock and wildlife that feed on these plants (Adriano et al., 1980; Gutenmann et al., 1976; Tolle et al., 1983). The concentrations of Se in some CFA-treated soils are close to or higher than those in some seleniferous soils, and Se concentrations in plants grown on these CFA-treated soils were similar to or

even higher than those grown in seleniferous soils in selenosis areas (Fang and Wu, 2004; He et al., 2017a; Zhang et al., 2007). Although Se concentrations in plants grown on CFA-treated soils may be below the level that results in chronic toxicity to animals, they can vary greatly among species, varieties, and tissues (Arthur et al., 1992a,c; Fang and Wu, 2004). In extreme cases, Se concentrations in plants grown on CFA landfill sites can reach a level highly toxic to animals, and elevated Se concentrations in animals have been observed after their consumption of plants grown on CFA-treated soils (Adriano et al., 1980; Gutenmann et al., 1976). Therefore, plant Se concentrations should be carefully monitored to avoid toxicity when using CFA for Se biofortification.

6.5 Macro- and micronutrient deficiency

Coal fly ash contains almost all essential macro- and micronutrients for plants, except N, and the low N content of CFA is an important constraint for its agricultural application (Basu et al., 2009; Jambhulkar and Juwarkar, 2009). Application of CFA at high doses may reduce N availability in the soil, and cause severe N deficiency, consequently suppressing plant growth and reduce crop yield (Pandey et al., 2009a). Furthermore, addition of unweathered CFA to soils can severely inhibit soil N cycling processes such as nitrification and N mineralization (Jala and Goyal, 2006). Application of CFA to soil may also cause lower K availability and reduced K concentrations in plants, due to low K concentrations in CFA, interaction of Mg, and possibly Ca, with K during plant ion uptake, and a possible "biological dilution effect" as well (Adriano et al., 1978; He et al., 2017a).

There are studies demonstrating that CFA is not an optimal source of P; application of CFA may not change plant–available P concentration in the soil, and high rates of CFA application may even reduce P availability in the soil, thus reducing P uptake by plants (Jambhulkar and Juwarkar, 2009; Pandey et al., 2009a;Shaheen et al., 2014; Yao et al., 2015). Adding CFA to a sandy loam with a low available P concentration did not correct P deficiency in corn as well as adding monocalcium phosphate did, suggesting that P in CFA is not readily available to plants. The unavailability of P in CFA may be due to the reaction of P with A1 and Fe, and the consequent formation of Fe-P and Al-P complexes, which adsorb P (Adriano et al., 1978; Elseewi et al., 1978). However, Yunusa et al. (2008) reported that increases in early vigor and seed yield are associated with enhanced uptake of P by canola grown on soil amended with an alkaline CFA. After the application of a lignite CFA

to an acidic red soil, the increase in maize yield was most likely associated with the increase in plant-available soil P concentration (Masto et al., 2013). An alkaine CFA obtained from the Jungar thermal power plant had a significantly higher total and plant-available P concentration than a loessial soil did, and the plant-available P concentration increased with increasing CFA application rate. In a 2-year pot experiment, the P concentration in alfalfa shoots in different cuts was generally increased when the CFA was applied to the loessial soil, and enhanced plant growth in CFA-amended soil was most likely due to increased P availability (He et al., 2017a). Therefore, application of CFA to soils does not invariably cause P deficiency; it is promising to use some CFAs as an alternative or supplement to commercial chemical P fertilizers to improve P nutrition in plants grown in low-P soils (He et al., 2017a; Pandey and Singh, 2010; Rautaray et al., 2003). Moreover, the environments in CFA-amended soils are suitable for the proliferation of P-solubilizing bacteria, which may contribute to enhanced P availability in the soil (Basu et al., 2009).

The availability of Cu and Zn declines with increasing soil pH (Marschner and Rengel, 2011). Application of alkaline CFA to soil can reduce Cu and Zn availability due to pH rise, and surface adsorption and precipitation may further reduce Cu and Zn availability in CFA-amended soils (Adriano et al., 1980; Masto et al., 2013). Some plants grown on CFA-amended soils show symptoms of Cu and Zn deficiency (Shaheen et al., 2014; Yao et al., 2015). However, the effects of CFA on Cu and Zn concentrations in plants depend on CFA type, plant species, and plant organs as well. Concentrations of Cu and Zn in the grain of fodder peas (*Pisum sativum*), autumn rye (*Secale cereale*), canola, and barley grown on CFA (pH 7.7–7.9) deposits were lower than those in the grain of the same species grown on unpolluted soils (Dželetović and Filipović, 1995). The CFAs (pH 7.9 and 8.0) on two CFA deposits had higher total Cu concentrations, but lower available Cu concentrations, and lower total and available Zn concentrations than those in the soil (pH 7.8) at the control site. Leaf Cu and Zn concentrations of *F. rubra* plants on the CFA deposits were higher than those at the control site, with leaf Cu concentrations being on the deficiency threshold and Zn concentrations being deficient on the CFA deposits (Gajić et al., 2016). When a CFA (pH 9.2) having a lower supply of total Cu and Zn, but higher supply of exchangeable Cu and Zn than a loessial soil (pH 8.7) was applied to the loessial soil, concentrations of exchangeable Cu and Zn in the soil increased, but Cu and Zn concentrations in shoots of alfalfa plants grown in the CFA-amended soil were lower than those of plants grown in the loessial soil in most cases (Fig. 4C and D), very likely due to the "biological dilution effects"

(He et al., 2017a,b). Application of unweathered CFA (pH 6.2–6.5) to soils (pH 5.0–5.9) significantly reduced Cu concentration in bush bean (*Phaseolus vulgaris*) plants, but did not markedly affect Cu concentrations in corn plants, and Zn concentrations in either corn or bush bean plants; however, application of CFA at high rates considerably increased HCl-extractable Cu and Zn concentrations (Adriano et al., 1978). For canola, application of CFA (pH 10.2) to soils (pH 6.4–6.6) did not affect Cu and Zn concentrations in stems, but increased Cu concentrations in leaves (Yunusa et al., 2008). Application of CFA (pH 5.6) to soil (pH 4.7) did not affect either Cu or Zn concentration in bermudagrass (*Cynodon dactylon*) leaves (Pathan et al., 2003). Application of CFA to an acidic sandy soil increased both Cu and Zn concentrations in plants of subterranean clover (*Trifolium subterraneum*) (Summers et al., 1998). For sugar beet (*Beta vulgaris*) plants, both Cu and Zn concentrations increased with increasing rate of CFA (pH 8.1) application to the soil (pH 7.7) (Singh et al., 2008). The availability of Zn in some CFAs is similar to that in commonly used fertilizers (El-Mogazi et al., 1988). Therefore, application of CFA to the soil does not invariably cause Cu and Zn deficiency in plants.

6.6 Potentially toxic trace element contamination and toxicity

Excessive amounts of undesirable PTEs such as, Hg, Cr, Pb, Cd, and U in CFAs could potentially contaminate the soil and water, and may cause toxicity to microorganisms, plants, animals, and humans (Haynes, 2009; Shaheen et al., 2014; Stefaniak et al., 2015). However, CFA application does not always increase the availability of PTEs and enhance their uptake by plants, or pose risks to human and animal health. Furthermore, although the uptake of PTEs can be significantly increased by CFA, their concentrations in plant tissues, especially in aboveground edible parts, are often within the acceptable level, partly because PTEs absorbed by the roots are mostly retained in the roots and are not readily translocated to the aerial parts (Ram and Masto, 2010).

The availability of Cr, Pb, and Cd decreases with increasing pH; in contrast, the availability of As increases with increasing pH and becomes maximal at pH >7 (Gajić et al., 2016; Jankowski et al., 2006; Ram and Masto, 2010). Concentrations of As in tissues of alfalfa grown on soil treated with high rates of CFA were above the level ($3.4\,\mu g\,g^{-1}$) considered toxic to sheep (Tolle et al., 1983). Both total and available As concentrations were significantly higher in the CFAs on two CFA deposits than in the soil at the control site, leaf As concentrations of *F. rubra* plants grown on the

CFA deposits were higher than those at the control site, and reached a toxic level (Gajić et al., 2016). Concentrations of Hg, Cr, and Cd in CFA are not deleterious to plants, and CFA treatment does not result in increased uptake of these elements by plants (Adriano et al., 1980). Application of CFA into sandy loam soils reduce Cr concentration in faba bean seedlings (Singh et al., 1997). A significant increase in Hg and Cd concentrations in subterranean clover grown in CFA-treated acidic sandy soils was reported, but such increase is within the range of natural variation levels (Summers et al., 1998). Application of CFA significantly increases As concentrations in bermudagrass, but does not affect Hg, Cr, Pb, and Cd concentrations in the same plants (Adriano et al., 2002). Application of CFA (pH 8.3) to a sandy loam acid lateritic soil (pH 5.3) resulted in reduced Cr concentration in rice grain and straw, due to an increase in soil pH (Rautaray et al., 2003). Concentrations of As, Hg, Cr, Pb, and Cd in leaves of bermudagrass are not affected when a sandy soil is treated with CFA (Pathan et al., 2003). Concentrations of Cr, Pb, and Cd in sugar beet increase significantly with increasing CFA application rate, but are all within the safe limits, and accumulation of these elements in sugarbeet grown in soil treated with 20% CFA would not pose any risk to human health (Singh et al., 2008). Concentrations of Cr, Pb, and Cd in plants grown on a CFA dump are below the toxicity threshold (Jambhulkar and Juwarkar, 2009). In the study of Pandey et al., 2009a, an unweathered CFA had a significantly higher Cd concentration than a garden soil, but the Cr concentration in the CFA was similar to that in the garden soil. Both Cr and Cd concentrations in roots, shoots, and seeds of pigeon pea (*Cajanus cajan*) increase with increasing application rate of unweathered CFA to garden soil, but a lower CFA-application rate (25%) ensures concentrations of Cr and Cd in edible parts are within the critical toxicity limits (Pandey et al. (2009a)). Patra et al. (2012) found that As and Pb concentrations in CFA-treated soil are well below the critical levels in soils for plant growth, and As and Pb are at a trace level in rice grains from CFA-treated soil.

Total As, Hg, Cr, Pb, Cd, and U concentrations in a CFA obtained from the Jungar thermal power plant are 1.9, 0.939, 3.8, 26.9, 0.07, and $4.7\,\mu g\,g^{-1}$, respectively, while those in a loessial soil were 9.7, 0.016, 24.0, 10.1, 0.08, and $0.5\,\mu g\,g^{-1}$, respectively. The CFA has significantly higher total and available Hg, Pb, and U concentrations, but markedly lower total and available As and Cr concentrations than the loessial soil. The CFA and the loessial soil have similar total Cd concentrations, but the available Cd concentration is considerably lower in the CFA than in the loessial soil

(H. He, unpublished work). In a 2-year pot experiment, As concentration in shoots of different cuts of alfalfa grown in a CFA–amended loessial soil was 0.3–1.5 (0.85 on average) μg As g^{-1} DM in the first year, while that in the control was $0.5\,\mu g$ As g^{-1} DM, but both decreased to a below-detection level in the second year (Fig. 5A), suggesting that the available As concentration declines with time, possibly due to plant uptake of As. However, Gajić et al. (2016) reported that available As concentrations in CFA deposits increase with time after the establishment of vegetation, possibly because the soluble organic matter in the CFA increases and inhibits the sorption of As on the surface of Fe oxides. Shoot Hg concentrations are not significantly
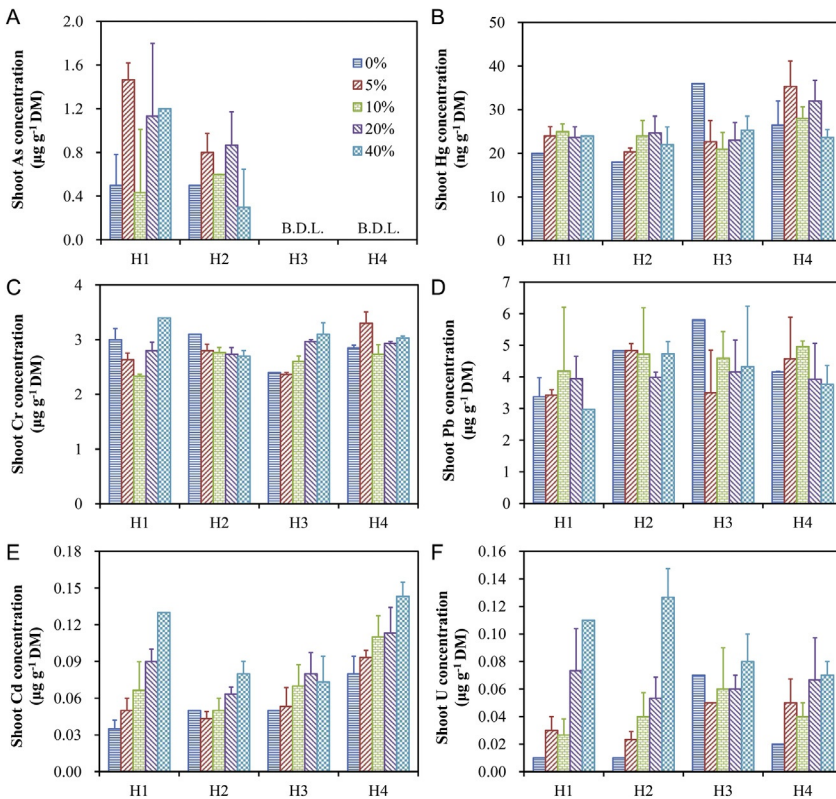

Fig. 5 Concentration of arsenic (As) (A), mercury (Hg) (B), chromium (Cr) (C), lead (Pb) (D), cadmium (Cd) (E), and uranium (U) (F) in shoots at four consecutive harvests (H1, H2, H3, and H4) of alfalfa (*Medicago sativa*) grown in a loessial soil amended with different rates of coal fly ash in a 2-year pot experiment. All data are presented as means + SD ($n = 3$). The details of the experimental design can be found in He et al. (2017a). Note: B.D.L. means below the detection limit of the analytical method.

affected by CFA treatments (Fig. 5B), but root Hg concentration increase markedly with increasing CFA application rate (H. He, unpublished work). Neither shoot nor root Cr concentrations are considerably affected by CFA treatments (Fig. 5C and H. He, unpublished work). Shoot Pb concentrations do not increase following CFA treatments (Fig. 5D), but root Pb concentrations increase in most cases when CFA is applied (H. He, unpublished work). Shoot Cd and U concentrations generally increase with increasing CFA-application rate (Fig. 5E and F), and there are similar trends for root Cd and U concentrations (H. He, unpublished work). Translocation factors of Hg, Cr, Pb, Cd, and U are all <1 (H. He, unpublished work), suggesting that most of these elements are retained in the roots, so that their toxicity in functional tissues and aerial edible parts of plants is avoided.

6.7 Organic contaminants and their toxicity

There are various complex organic compounds such as polycyclic aromatic hydrocarbons (PAHs), and polychlorinated biphenyls (PCBs) present in CFA (Gohda et al., 1993; Ribeiro et al., 2014; Rose and Rippey, 2002; Sahu et al., 2009). The levels of PAHs and PCBs in CFA are generally low (Shaheen et al., 2014). However, if CFA is applied to the soil in excessive amounts, CFA-borne PAHs and PCBs, which are persistent toxic substances, can adversely impact soil, water, and plants, and pose a serious risk to the environment, human and animal health, and biodiversity (Li et al., 2014a; Ribeiro et al., 2014). Therefore, CFA should be applied with caution; PAHs and PCBs as pollutants should be monitored in the environment, environmental standards for PAHs and PCBs in CFA should be established, and guidelines for PAHs and PCBs in land-use limit should be developed (Li et al., 2014a). The effects of CFA-borne PHAs and PCBs on soil biota, their uptake by plants, and their persistence in the soil have not received much scientific attention, and warrant integrative assessment (Shaheen et al., 2014).

6.8 Radioactivity in soil and plants

Radionuclides such as U- and Th-series, ^{40}K, ^{226}Ra, ^{210}Pb, ^{228}Ra, ^{134}Cs and ^{137}Cs, ^{222}Ru and ^{220}Ru are present in CFAs (Aycik and Ercan, 1997; Bauman and Horvat, 1981; Dželetović and Filipović, 1995; Noli et al., 2017; Papastefanou, 2010; Tadmore, 1986). However, since most CFAs do not have significantly higher levels of radionuclides than soils or rocks,

application of CFA does not necessarily cause soil and water contamination with radionuclides (Zielinski and Finkelman, 1997).

The radioactivity of ^{134}Cs and ^{137}Cs, and total gamma activity in grains of various crops grown on CFA deposits are of the same order as the natural background without pollution, and they are not an obstacle to use the surface of the CFA deposit for crop production (Dželetović and Filipović, 1995). Mittra et al. (2005) reported that CFA-treated soil shows lower radioactivity of ^{226}Ra, ^{228}Ac, and ^{40}K, but higher radioactivity of ^{137}Cs than the un–treated soil. Application of a high dose of CFA (200 t ha^{-1}) increased radioactivity levels with respect to γ-emitters ^{220}Ra, ^{228}Ac, and ^{40}K in mine spoil, which were above the control values, but the levels of the radionuclides were well within permissible limits (Ram et al., 2006). There were slight increases in the radioactivity levels of ^{226}Ra and ^{228}Ac, and a substantial increase in ^{40}K in the grains and straws of various crops grown on mine spoil amended with 100 and 200 t ha^{-1} CFA, but the levels of the radionuclides in crop produce were within the range measured in produce grown on land without CFA and fell well within permissible limits, and the significant increase in ^{40}K was possibly due to the application of chemical fertilizers containing K (Ram et al., 2006). For the use of CFA for soil amendment, the variation in the concentrations of radionuclides such as ^{226}Ra, ^{232}Th, and ^{40}K in soil, CFA, and crop produce depend on the types of soil and CFA, mobilization of the radionuclides from soil/CFA to plants, and the interactions between radionuclides and soil. The concentrations of radionuclides in soil, CFA, and crop produce are generally within the permissible limits (Tripathi et al., 2014).

6.9 Other disadvantages, potential negative effects and hazards

In addition to the disadvantages, potential negative effects and hazards mentioned above, excessive S in CFA can also be toxic to plants and restrict the application of CFA for Se biofortification (Shaheen et al., 2014). High rates of CFA can inhibit microbial activity in the soil, and consequently reduce N mineralization, nitrification, and activity of urease and phosphatase enzymes (Arthur et al., 1984; Haynes, 2009; Lim and Choi, 2014; Nayak et al., 2015). However, Schutter and Fuhrmann (1999, 2001) found no detrimental effects of CFA amendment on the microbial community; instead, CFA amendment enhanced the activity of some fungi and bacteria, the lack of detrimental effects were attributed to improved soil physicochemical properties and enhanced plant growth. The application of CFA to an acidic

soil significantly improves the physicochemical properties of the soil, and increases the population density of some beneficial soil microorganisms such as phosphate-solubilizing-bacteria, Actinomycetes, *Azotobacter*, and AMF (Parab et al., 2015). The effects of CFA on soil microbial activity vary among types of soil (Wong and Wong, 1986).

7. Measures for efficient use of CFA for selenium biofortification and hazard reduction and prevention

The potential negative effects and hazards listed in the previous section can be mitigated by applying appropriate amounts of CFA, and most constraints can be handled by taking proper measures, provided that the specifc characteristics of the CFA and soil are considered, and the suitability of using a specific CFA for the amendment of a specific soil is carefully evaluated, and an appropriate CFA-application rate is worked out beforehand (Ram and Masto, 2014; Shaheen et al., 2014). There are a few measures to take to use CFA efficiently for Se biofortification, and to reduce and prevent potential hazards.

7.1 Applying suitable CFA to soil at appropriate rates

Whether a specific CFA is suitable for the amendment of a specific soil depends on the characteristics of the CFA and that of the soil, including pH, EC, organic matter content, concentrations of essential plant nutrients, PTEs, organic pollutants, and activity of radionuclides (Ram and Masto, 2010; Shaheen et al., 2014). It is recommended to use CFA containing low levels of elements causing potential toxicity, including B, Mo, As, Hg, Cr, Pb, and Cd for agricultural purpose. Weathered CFA is preferred to unweathered CFA, due to lower EC, and lower levels of B, Mo in weathered CFA (Haynes, 2009; Jala and Goyal, 2006; Yunusa et al., 2012). The problems of salinity, toxicity of B, Mo, Se, S, toxic metals and metalloids, organic pollutants, and radioactivity, as well as macro- and micronutrient deficiency can be minimized by applying CFA at appropriate rates (Pandey and Singh, 2010; Ram and Masto, 2014).

7.2 Co-application or co-composting of CFA with organic matter-rich materials, and vermicomposting

Because CFA contains little or no N and organic C, co-application of CFA with organic matter-rich materials such as poultry and animal manure, sewage sludge, press mud, and biochar is considered better than CFA alone. Besides

increasing the contents of N, P, and organic C, co-application of CFA with these materials has a few other advantages, including reducing the mobility and bioavailability of PTEs, buffering soil pH, increasing microbial activity, improving the general health of the soil, and enhancing plant growth (Haynes, 2009; Masto et al., 2013; Ram and Masto, 2014; Shaheen et al., 2014). Furthermore, the co-composting and vermicomposting technology can be used to increase the bioavailability of N, P, and organic C, and reduce the toxicity of PTEs, provided suitable materials are selected and appropriate proportions of each component are worked out (Belyaeva and Haynes, 2009; Bhattacharya et al., 2012). Among the various co-amendment materials, farm manure and sewage sludge are more effective, and farm manure is considered the most promising amendment used along with CFA. It is best to seek locally available fitting blending materials to exploit the most benefits from their synergistic interaction (Ram and Masto, 2014; Yao et al., 2015).

7.3 Inoculation with beneficial microbes

Microbial activity is important for a series of soil reactions and functions, including organic matter decomposition, humus formation, nutrient cycling, aggregate formation and stabilization. Therefore, development of an active and diverse microbial community will increase the suitability of CFA-treated soil for plant growth (Haynes, 2009). Inoculation of CFA-tolerant strains of *Rhizobium* bacteria (symbiotic N_2-fixing bacteria associated with legumes) has a positive role in enhancing plant growth through increasing N supply (Chaudhary et al., 2011). Arbuscular mycorrhizal fungi (AMF) can increase P uptake, but reduce uptake of Se and PTEs by plants or translocation of these elements from roots to shoots (Chen et al., 2007; Munier–Lamy et al., 2007). Duran et al. (2013) found that selenobacteria increase Se uptake by wheat plants and Se concentration in wheat grains, and co-inoculation of selenobacteria (Se-tolerant bacteria) and AMF further increase plant Se uptake and grain Se concentration, suggesting a synergistic effect between the selenobacteria and AMF, and a potential application of these rhizosphere microbes for Se biofortification (Acuna et al., 2013). However, the effects of rhizosphere microbes on plant Se uptake and translocation depend not only on the species and strains of microbes, but also on the species and varieties of plants (Lindblom et al., 2013). A biotechnological approach to using CFA for Se biofortification including inoculation with beneficial microbes to enhance plant growth and Se uptake warrants further investigation (Haynes, 2009; Lindblom et al., 2013).

7.4 Selection of suitable plant species and varieties, and genotypes

The capacity to accumulate Se in plant tissues vary greatly among plant species and varieties (Terry et al., 2000; White, 2016). Fleming (1961) studied Se in Irish soils and plants, and found that crop plants in the family of Brassicaceae, Liliaceae, and Fabaceae had higher Se concentrations than plants in the family of Asteraceae, Poaceae, and Apiaceae did. Miltimore et al. (1975) reported that Se concentrations in legumes and wheat were much higher than those in corn grown in the same region. Arthur et al. (1992c) found that leguminous species growing on CFA landfills generally had higher Se concentrations than grasses did. For efficient use of CFA for Se biofortification, it is important to select suitable plant species and varieties that can accumulate Se at appropriate levels. As a complementary approach to agronomic biofortification using Se-fertilizers or Se-rich natural materials or wastes, genotype selection for enhanced Se accumulation in edible plant parts is receiving increasing interests (White and Broadley, 2009; Zhu et al., 2009). The finding that Se-accumulators may have Se-specific transporters that enable them to preferentially take up Se over S suggest that it is beneficial to develop crop genotypes with improved Se accumulation and tolerance traits through conventional breeding or genetic engineering (Cabannes et al., 2011; DeTar et al., 2015; El Mehdawi et al., 2015; White, 2016; White et al., 2004; Zhang et al., 2014; Zhu et al., 2009). Furthermore, it is also necessary to consider plants that are better at accessing P from CFA using a P-mining strategy, plants such as lupins (Lambers et al., 2013; Pearse et al., 2006, 2007), acacias (He et al., 2012), alfalfa (He et al., 2017b; Pang et al., 2010; Suriyagoda et al., 2012), lots of other legumes and canola (Kidd et al., 2016; Pearse et al., 2006), and *Macadamia* (Hue, 2009). These can mobilize sparsely soluble P such as Fe-P, Al-P, and Ca-P by releasing significant amounts of carboxylates into the rhizosphere are promising candidates.

7.5 Blending selenium-rich plant materials with low-selenium diet, or using selenium-rich plant materials as a dietary selenium supplement

Selenium-rich plant materials that are produced on CFA-treated soils may cause Se toxicity to animals and humans if consumed at high doses. However, they should not be considered as a problem, as they can be blended with low-Se feed or food at appropriate rates to increase the dietary

supply of Se in Se-deficiency areas, in a similar manner to blending UK-grown low-Se wheat with North American high-Se wheat to increase the Se uptake by the UK population (Hart et al., 2011). Corn grain with increased Se concentration produced on soil amended with CFA in New York was used to replace supplemental Se added to poultry feed diets (Combs et al., 1980). High-Se plant material can be used as a Se supplementation at rational doses to provide the required amount of Se for most animals and humans (Suyama et al., 2007; Vonderheide et al., 2002). Generally, organic forms of Se are more bioavailable and less toxic than inorganic forms such as selenates and selenites (Lyons et al., 2007; Tinggi, 2003; White, 2016; Zhu et al., 2009). Because a significant proportion of Se in plants is present in organic forms, the use of Se-rich plant materials produced on CFA-treated soils may provide more benefits than other forms of Se supplement such as inorganic mineral supplementation for long-term population-wide Se supplementation strategies (Hart et al., 2011; Kieliszek and Blazejak, 2013; Tsai et al., 2013).

8. Conclusions and future prospects

Most CFAs are rich in Se and can increase Se bioavailability when applied to soil, thus increasing plant uptake of Se. Using CFA as a soil amendment can also improve the physicochemical properties of the soil, including soil texture, bulk density, water-holding capacity, pH, and supply a range of macro- and micronutrients, thereby enhancing plant growth and increasing crop yields when CFA is applied to soil at appropriate rates. Application of CFA, especially unweathered CFA, to soils at high doses may have some disadvantages, and could have negative effects on the environment and bring undesirable hazards, including soil salinity, contamination of soil, water, and the food chain with toxic substances such as B, Mo and Se, toxic metals and metalloids, and organic pollutants. It may also induce macro- and micronutrient deficiency in plants, increase radioactivity and cause S toxicity, and inhibit microbial activity. However, these potential negative effects can be mitigated, and the potential hazards can be reduced or prevented by applying appropriate amounts of CFA. Furthermore, there are a few possible measures to efficiently use CFA for Se biofortification and hazard reduction and prevention, including (1) co-application or co-composting of CFA with organic matter-rich materials, or using a vermicomposting technology to increase the availability of N, P, and organic C; (2) innoculating plants with beneficial microbes to facilitate Se uptake and

translocation; (3) selecting suitable plant species, varieties, and genotypes for efficient Se uptake and accumulation; and (4) supplementing Se-rich plant materials produced on CFA–amended soils to a low–Se diet, or using Se-rich plant materials as a dietary Se supplement to provide enough dietary Se and avoid Se toxicity in humans and animals. Therefore, it is very promising to use Se-rich CFA as a soil amendment for Se biofortification, provided that the specifc characteristics of the CFA and soil are considered, and the CFA meets the contaminants standards for soil application. Appropriate CFA-application rates should be prudently worked out beforehand, considering the cost and benefit and various environmental limits, and relevant hazard reduction and prevention measures must be taken. Continuous in-depth research under field conditions in a small trial area is necessary to evaluate the feasibility and long-term safety of using CFA for Se biofortication, relevant guidelines on proper use of CFA for Se biofortication should be proposed on the basis of multidisciplinary research, in order to promote appropriate disposal of CFA as a waste material as well as its beneficial reuse.

Acknowledgments

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