Journal of Environmental Management 197 (2017) 428–439

Contents lists available at ScienceDirect

Journal of Environmental Management

journal homepage: www.elsevier.com/locate/jenvman

Research article

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

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A R T I C L E I N F O

Article history:
Received 27 November 2016
Received in revised form
3 April 2017
Accepted 8 April 2017
Available online 12 April 2017

Keywords:
Alkaline and calcareous soil
Macronutrients
Micronutrients
Selenium
Soil amendment

A B S T R A C T

Coal fly ash (CFA) is a problematic solid waste all over the world. One distinct beneficial reuse of CFA is its utilization in land application as a soil amendment. A pot experiment was carried out to assess the feasibility of using CFA to improve plant growth and increase the supply of plant-essential elements and selenium (Se) of a loessial soil for agricultural purpose. Plants of alfalfa (*Medicago sativa*) were grown in a loessial soil amended with different rates (5%, 10%, 20% and 40%) of CFA for two years and subjected to four successive cuttings. Dry mass of shoots and roots, concentrations of plant-essential elements and Se in plants were measured. Shoot dry mass and root dry mass were always significantly increased by 5%, 10% and 20% CFA treatments, and by 40% CFA treatment in all harvests except the first one. The CFA had a higher supply of exchangeable phosphorus (P), magnesium (Mg), copper (Cu), zinc (Zn), molybdenum (Mo), and Se than the loessial soil. Shoot P, calcium (Ca), Mg, Mo, boron (B), and Se concentrations were generally markedly increased, but shoot potassium (K), Cu, and Zn concentrations were generally reduced. The CFA can be a promising source of some essential elements and Se for plants grown in the loessial soil, and an application rate of not higher than 5% should be safe for agricultural purpose without causing plant toxicity symptoms in the studied loessial soil and similar soils. Field trials will be carried out to confirm the results of the pot experiment.

1. Introduction

Coal fly ash (CFA) is a by-product of coal combustion in thermal power plants; it is generated in huge quantities every year, and has been regarded as a problematic solid waste all over the world. Coal has been and continues to be the largest source of electric power production in the world. To meet the ever-increasing electricity demand, global coal consumption has been increasing considerably year-by-year and is expected to continue increasing; consequently, the amount of CFA generated annually will keep rising. As the largest coal-consuming country in the world, the annual CFA generation of China was about 0.6 billion tons by 2015, ranking first in the world. The storage and disposal of such a huge amount of CFA requires vast areas of land. CFA landfills and disposal ponds have many negative impacts on the ecosphere, and have raised serious environmental concerns (Pandey and Singh, 2010; Yao et al., 2015). In comparison with landfilling, beneficial reuse of CFA is a more economic and environmentally-sustainable alternative option for CFA disposal. The beneficial utilization rate of CFA has been increasing globally in recent years. Current and potential utilization of CFA includes its use in soil amendment, construction industry, ceramic industry, catalysis, depth separation, zeolite synthesis, valuable metal recovery, etc. (Blissett and Rowson, 2012; Yao et al., 2014, 2015).

When added to soil, CFA may improve the physicochemical properties of soil, including soil texture, water-holding capacity, and pH (Jala and Goyal, 2006; Blissett and Rowson, 2012). Coal fly

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http://dx.doi.org/10.1016/j.jenvman.2017.04.028

ash contains a series of essential elements for plant growth, including macronutrients such as phosphorus (P), potassium (K), sulfur (S), calcium (Ca), and magnesium (Mg), as well as micronutrients such as iron (Fe), manganese (Mn), copper (Cu), zinc (Zn), molybdenum (Mo), nickel (Ni), and boron (B). When applied appropriately, CFA can be a valuable source of nutrient supplementation to improve soil fertility (Pandey and Singh, 2010; Yao et al., 2015). A number of studies have demonstrated that application of CFA to soils promoted plant growth and greatly increased yield of crops such as alfalfa (*Medicago sativa*), barley (*Hordeum vulgare*), sunflower (*Helianthus* sp.), and groundnut (*Arachis hypogaea*) (Jala and Goyal, 2006). Greater yield of crops has been attributed to increased availability of some macro- and micronutrients in CFA-amended soils (Shaheen et al., 2014). However, Zn supply was reduced following application of CFA to soil in some cases, and some plants grown in CFA-amended soils showed Zn deficiency symptoms, possibly because Zn availability decreased when soil pH was increased (Singh et al., 2008; Shaheen et al., 2014; Yao et al., 2014). In addition, some elements such as Mo, B, and Se are often present in considerable amounts in CFA, their concentrations in plants grown in CFA-amended soils are consistently higher than those grown in soils without CFA application, and can cause toxicity to plants and animals, thus restricting the utilization of CFA for agricultural purpose (Pandey and Singh, 2010; Shaheen et al., 2014).

Many studies have demonstrated that CFA is one of the cheapest and widely available waste materials which have enormous potential to improve degraded soils for agriculture and forestry (Ram and Masto, 2014; Shaheen et al., 2014). However, characteristics of CFAs vary greatly, depending on factors such as feed coal and combustion conditions, the suitability of a particular CFA for the amendment of a specific soil should be carefully evaluated before it is applied (Ram and Masto, 2014). When applied in appropriate amounts and considering the likely changes in soil pH, CFA can be a useful source of nutrient supplementation and help alleviate the deficiency of some nutrients in soils (Mittra et al., 2005; Pandey and Singh, 2010; Shaheen et al., 2014). As the pH and concentrations of plant-available elements in CFA-amended soils usually change with the time after CFA application (Shaheen et al., 2014), it is necessary to study the accumulation of mineral elements by plants grown in CFA-amended soils at different time to determine the appropriate CFA application rate for agricultural purpose.

On the Loess Plateau in China, alfalfa (*Medicago sativa* L.) is an important perennial herbaceous forage legume which has been cultivated for at least 150 years, and it is an important component of the agroecosystem (Deng et al., 2014; Fan et al., 2015). The most widely distributed soils on the Loess Plateau are loessial soils, which are typically alkaline and calcareous (Catt, 2001), and the productivity of alfalfa is often limited by deficiency of some mineral nutrients such as P in these soils (Fan et al., 2015). Furthermore, the Loess Plateau lies in the Se-poor belt, an area in which Se concentrations in soil are extremely low, and diseases such as Kashin–Beck disease (a chronic bone and cartilage disease) and Keshan Disease (a chronic heart disease) which are related with low Se intake used to be prevalent in this area (Blazina et al., 2014). Agronomic biofortification of various food crops with Se could provide an appropriate strategy to increase the intake of Se by animals and humans, and address Se malnutrition problem effectively (Poblaciones et al., 2014; Malagoli et al., 2015). One of the agronomic practices for Se biofortification is to increase Se bioavailability in soils by applying Se fertilizers (Poblaciones et al., 2014; Smolen et al., 2016). Coal fly ash is often rich in some mineral nutrients and Se, and can increase concentrations of some mineral nutrients and Se in plants when it is applied to soils (Shaheen et al., 2014). It is not clear whether CFA can be applied to the loessial soil to improve the supply of plant-essential elements for alfalfa. The feasibly of using CFA in soil amendment for Se biofortification warrants detailed assessment.

In the present study, we amended a type of loessial soil, a calcareous and nutrient-poor soil on the Loess Plateau, China, with different rates of CFA, and carried out a pot experiment to grow alfalfa in the CFA-amended loessial soil. The objective was to investigate the effects of CFA application on plant growth of alfalfa and accumulation of plant-essential elements and Se at different harvest time, and to assess the feasibility of using CFA to improve the supply of plant-essential elements and Se of the loessial soil, an alkaline and calcareous soil, for agricultural purpose. We hypothesized that plant growth would be promoted at lower CFA application rates and inhibited at higher CFA application rates, and the accumulation of some plant-essential elements and Se would be increased with increasing CFA application rate.

2. Materials and methods

2.1. Substrate preparation

The loessial soil used for this study was obtained from the northern edge of the Loess Plateau by collecting the 0–40 cm surface soil. Fresh CFA was obtained from an ash collector at the Jungar Thermal Power Plant, which is close to the site where the loessial soil was collected, and located in the Jungar Banner, Inner Mongolia, China. Both the loessial soil and CFA were collected in October 2013, air-dried, passed through a 2-mm sieve, and analyzed for selected physicochemical properties. Soil particle size distribution was measured by a laser diffraction particle size analyzer (Lamorski et al., 2014), pH and electrical conductivity (EC) were measured in a 1:5 soil:water (w:v) suspension, field capacity was measured using the indoor cutting-ring weighing method, soil organic carbon was determined using the potassium dichromate titrimetric method, ammonium-nitrogen (NH_4^+–N) and nitrate-nitrogen (NO_3^-–N) were extracted by a 2 M KCl [soil:solution = 1:10 (w:v)] and then analyzed by a segmented-flow analyzer. Total concentrations of P, K, Ca, Mg, S, Fe, Mn, Cu, Zn, Ni, Mo, B, and Se were analyzed using inductively coupled plasma mass spectrometry (ICP-MS, ELAN 9000, PerkinElmer Instruments, Shelton, CT, USA) after a modified aqua regia digestion (Reimann et al., 2015). A certified soil reference material STD DS 10 was used for data quality control, the expected values, measured values, and recovery rates were provided in Table S1, with the recovery rates of all measured elements ranging between 92.2% and 109.8%.

The CFA was applied to the loessial soil at different rates, i.e. 0%, 5%, 10%, 20%, and 40% (weight ratio), and mixed with the loessial soil thoroughly. Non-transparent PVC tubes which were of 11-cm diameter and 40-cm height with a sealed bottom were used as the containers for the pot experiment. At first, the bottom of each pot was covered with some gravel, and then each pot was filled with 3 kg of the loessial soil-CFA mixture. For each treatment, 33 pots were prepared separately, without supplying any additional fertilizer throughout the experiment. The substrate was watered to 21% gravimetric water content (60% of the field capacity of the loessial soil) weekly with deionized water, and incubated at room temperature for 100 days.

2.2. Plant cultivation and harvest

A two-year pot experiment was carried out in a transparent rain shelter at ambient temperature in the Institute of Soil and Water Conservation, Yangling, Shaanxi, China. Seeds of alfalfa were first sterilized in 30% H_2O_2 solution for 5 min, then rinsed with cold tap water three times and soaked in cold tap water overnight. For each