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Macro and Microminerals of four Cuphea genotypes grown across the upper Midwest USA☆

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ABSTRACT

Cuphea seed oil can be used for many purposes from motor oil and cosmetic components to jet fuel, because its seeds are a rich source of medium-chain fatty acids (C8:0 to C14:0). Processing cuphea oil to biofuel and other bioproducts of high quality can depend on the heavy metal content of its seed. However, little is known about the macro and micromineral content of its seed. The objective of this study was to evaluate mineral content of cuphea, especially heavy metal content for processing the oil into biofuels/bioproducts and to determine how this may differ across environments. Four cuphea genotypes were evaluated; two of which were semi-domesticated genotypes [PSR23 and HC-10 (*Cuphea viscosissima* Jacq. × *C. lanceolata* W.T. Aiton)] and two were wild species (*Cuphea wrightii* and *C. viscosisima* (VS-6-CPR-1). The study was conducted at four locations in North Dakota (ND), Minnesota (MN), Iowa (IA), and Illinois (IL). The soil was a Perella silty clay loam at Prosper, ND, a Barnes loam at Morris, MN, a Clarion loam at Ames, IA, and an Osco silt loam at Macomb, IL. PSR23 and HC-10 were directly-seeded in the field and the two wild species were transplanted. All cuphea seeds contained some heavy metals. Although phosphorus (P) and potassium (K) were equally fertilized at all sites, the concentrations of P and K in seeds of PSR23 and HC-10 tended to be lower at the MN site than IA and IL sites, while the lowest P concentration was observed at the MN site for VS-6 and *C. wrightii*. Among calcium (Ca), magnesium (Mg), and sodium (Na) in cuphea seeds, sodium had the lowest concentration. The average concentrations for microminerals ranged from 40 to 53 mg kg^{-1} for zinc (Zn), from 11.9 to 14.1 mg kg^{-1} for copper (Cu). These concentrations are low compared to those found in many livestock feeds. Lead (Pb) and vanadium (V) were sporadically observed at a few locations. Cobalt (Co) was only detected for VS-6 at IA and *C. wrightii* at IA and MN, while cadmium (Cd) was only found for HC-10 at ND, PSR23 at IA, and *C. wrightii* at ND. These results suggest that the concentrations of macro cuphea seeds varied by genotype and environment. This information will be useful for those industries interested in processing cuphea seed oil for manufacturing biofuels, cosmetics, and other specialty chemicals.

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1. Introduction

Cuphea is known as a promising industrial oilseed crop, and cuphea (PSR23) is grown in the upper Midwest USA has provided evidence for this by producing seed oil that is rich in medium-chain fatty acids (Gesch et al., 2006). Also, its seed oil is highly desirable for a wide range of products from personal care goods such as, cosmetics, detergents, and lubricants to liquid biofuels (Brown et al., 2007). cuphea oil that is rich in caprylic (C8:0) and capric acids (C10:0) has similar fuel properties to No. 2 diesel without being converted to methyl esters (Geller et al., 1999). Moreover, the chain lengths of cuphea oil fatty acids are similar in length to that of hydrocarbon chains in jet fuels (Kim et al., 2011). Cermak and Isbell (2004) reported that cuphea-oleic estiolides synthesized from PSR23 cuphea oil make an excellent engine lubricant, because of their good low temperature properties.

Cuphea oil could supplement coconut (*Cocos nucifera* L.) and palm kernel (*Elaeis guineensis* Jacq.) oils for chemical manufacturing. Refined crude oil has similar chemical characteristics to cuphea oil. Many studies show that minerals of crude oil could affect the quality of products, deteriorate the efficiency of oil refining processes, and pollute the environment. For example, Souza et al. (2006) reported that vanadium (V) is a poisonous catalyst and

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causes corrosion in furnaces and boilers during the refining oil processes and Ni and V emissions have been strictly controlled due to their mutagenic and carcinogenic potential. The presence of Nickel (Ni), V, Fe, and Cu can influence the activity of catalysts causing a yield reduction of gasoline, and the presence of V, K, Mg, and Ca may lead to ash deposits on turbine rotors, so that it may reduce the efficiency of heat transfer and cause corrosion (Speight, 2001). Mozaffari (2000) reported that K, Na, and Ca are minerals that are notorious for increasing slag in engines. Copper, Fe and Zn metals can also be partially transferred to fuels, resulting in decreased quality and performance. Undesirable minerals including Cd and Na may cause an additional disposal challenge, because they can clog burners or decrease combustion efficiency (Halgerson et al., 2004). Similarly, the inorganic minerals in cuphea oil, potentially including metals, may cause issues when cuphea oil is processed into biofuels. Thus, understanding the mineral composition of cuphea seed will be useful in determining the efficiency of refining it for bioproducts and determining its potential to be an environmentally friendly biofuel feedstock.

Many metals in cosmetics and personal care products are forbidden in the United States, because of issues related with human health and safety. For instance, lead is a proven neurotoxin, which may build up in the body over time and the U.S. Centers for Disease Control and Prevention (CDC, 2014) says "no safe blood lead level has been identified". FDA reported that lead levels in lipsticks ranged from 0.09 to 3.06 mg kg^{-1} in 2009 and another FDA study showed that lead in 400 lipsticks were as high as 7.19 mg kg^{-1}. However, the problem is that their natural impurities are not under regulation (Federal Food, Drug and Cosmetic Act, 2014).

Furthermore, some of the byproducts from processed seed are used for animal feeds. Typical byproducts include distiller's dried grains from corn (*Zea mays* L.) and protein from soybean [*Glycine max* (L.) Merr.] meal, which can contain high phosphorus levels (Kalscheur et al., 2012; U.S. Grains Council, 2012). The U.S. Grains Council (2012) reported that the highest tolerable level for S in feedlot diets is 0.40% (DM basis). Sulfur is reduced by hydrogen sulfide by ruminal bacteria, which is toxic, eventually causing polioencephalomalacia (PEM). Conversely, high sulfur may be beneficial for swine, because it can help avoid metabolic oxidation imbalance. Young animals deficient in K may fail to grow normally and the concentration of Na in cells is 20–30 times less than K concentrations in cells (Leeson et al., 1998). Magnesium can improve the digestibility of feed and it helps hens increase egg production (Gaál et al., 2004). Plant tissue analysis of minerals is a critical tool for evaluating the nutritional status and quality of crop products (Hansen et al., 2013). Minerals contained in cuphea seeds might be important in the processing for biofuels and bioproducts. Although cuphea is being developed as a non-food source, its byproduct may have nutritional benefits for animal feeds (Sink and Lochmann, 2007). However, little is known about the macro and microminerals of cuphea seeds. The objective of this study was to evaluate mineral content of cuphea, especially heavy metal content for processing the oil into biofuels/bioproducts.

2. Material and methods

2.1. Plant culture

This research was conducted in 2007 at four locations throughout the upper Midwest USA. The locations were Prosper, ND (longitude–latitude; 97°1′W, 46°5′N), Morris, MN (longitude–latitude; 95°5′W, 45°3′N), Ames, IA (longitude–latitude; 93°3′W, 42°2′N), and Macomb, IL (longitude–latitude; 90°4′W, 40°3′N). The soil series was a Perella silty clay loam (fine-silty, mixed, superactive, Typic Endoaquolls) for Prosper, ND, a Barnes loam soil (fine-loamy, mixed, superactive, frigid Calcic Hapludolls) for Morris, MN, a Clarion loam soil (fine-loamy, mixed, superactive, mesic Typic Hapludolls) for Ames, IA, and an Osco silt loam soil (fine-silty, mixed, superactive, mesic Typic Argiudolls) for Macomb, IL. Four cuphea genotypes were planted at each study site. Seeds of PSR23 and HC-10 cuphea used for planting were collected in 2006 in West-Central MN and seeds of the *C. wrightii* (accessin: Ames 17789), and VS-6-CPR-1 (here after referred to as VS-6) (accession: PI 574621; Tagliani et al., 1995) were obtained from the USDA-ARS-North Central Regional Plant Introduction Station in Ames, IA.

The experimental design was a randomized complete block design with four replications. cuphea PSR23 and HC-10 were direct seeded, while *C. wrightii* and VS-6 were transplanted from seedlings. Both *C. wrightii* and VS-6 were pregerminated before transferring to 72-well trays filled with a commercial potting soil mix (Miracle-Gro Potting Mix Scotts Company, Marysville, OH) and grown in a greenhouse in Morris, MN under day/night temperatures of 21/18 °C. The seedlings were transplanted to the field on the same day that PSR23 and HC-10 were directly-seeded. The seedlings were transplanted approximately 50 mm apart within rows and the plant population density was approximately 89,100 ha^{-1}. Soil samples from the 0–15 and 15–30 cm depth were taken from plots to analyze bulk density, soil pH (1:10), and electrical conductivity (EC). The soils at all four locations were loam soils and the soils at both the IA and ND sites had high clay contents and thus, had poor drainage characteristics, whereas, the MN and IL soils had much better drainage. Detailed information with regards to cultural management of plants can be found in Kim et al. (2011). The macronutrients N, P, K, and S were broadcast at rates of 90, 34, 45, and 34 kg ha^{-1} for N, P, K, and S, respectively. Nitrogen was added primarily as urea, P as diammonium phosphate, K as potash, and S as elemental sulfur. Both macronutrients and trifuluralin [2,6-dinitro-N,N-dipropyl-4-(trifuluoromethy)aniline] at 1.1 kg ha^{-1} active ingredient were incorporated into the soil at least 2 days before planting. The planting dates were May 7 in IL, May 14 in IA, May 20 in MN, and May 16 in ND. Supplemental irrigation with an overhead sprinkler was applied at 35, 28, and 32 mm on 6 July, 24 July, and 9 August, respectively, in 2007 only at the MN site, because plants showed symptoms of drought stress. Growing degree days (GDD) from planting to harvest were from 1114 at the most northerly site (ND), followed by 1214 at MN, 1410 at IA, and 1561 at the most southerly site (IL). GDD used a lower limit temperature of 10 °C with no upper limit temperature.

2.2. Plant samples

At physiological maturity, plant samples including seeds and stover from 2.64 m^2 in each plot were hand-harvested. After drying, seeds and stover yields were determined. Subsamples were dried and analyzed for the macro and microminerals. For seed analysis, seed of two replications was used for wet digestion and one analysis was performed per replication. cuphea seeds were wet-digested, using a Mars Xpress Microwave System (CEM Corp., NC, USA), and sample preparation was performed according to note XprAG-1 of the US-EPA methods (US-EPA 5051 methods). A Varian Vista-Pro CCD (Charge Coupled Device, Varian Inc., Palo Alto, CA, USA) with simultaneous ICP-OES (inductively coupled plasma–optical emission spectroscopy) instrument was used for the macro and microminerals analysis. For cuphea seed sample analysis, a cross-flow pneumatic nebulizer operated at 1 L argon/min at 20 psi was used. The working wave lengths for individual minerals were listed below: Cu 324.8 nm, Zn 213.9 nm, Pb 220.4 nm, and Cd 214.4 nm. Detection limits for Pb, Cu, Zn, and Cd were 0.1 mg/L, 0.02 mg/L, 0.1 mg/L, and Cd 0.02 mg/L, respectively. Five aqueous standard solutions in 2% (v/v) HNO_3 were used for performing the calibration. A commercial multi-element standard stock solu-