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Concentration of cadmium in cacao beans and its relationship with soil cadmium in southern Ecuador

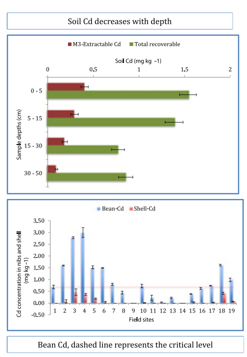
E. Chavez [a,d], Z.L. He [a,*], P.J. Stoffella [a], R.S. Mylavarapu [b], Y.C. Li [c], B. Moyano [d], V.C. Baligar [e]

[a] University of Florida, Institute of Food and Agricultural Science, Indian River Research and Education Center, Fort Pierce, FL 34945, USA
[b] University of Florida, Institute of Food and Agricultural Science, Soil and Water Science Department, Gainesville, FL 33611, USA
[c] University of Florida, Institute of Food and Agricultural Science, Tropical Research and Education Center, Homestead, FL 33031, USA
[d] Escuela Superior Politecnica del Litoral, Centro de Investigaciones Biotecnologicas del Ecuador, Guayaquil, Guayas, Ecuador
[e] United State Department of Agriculture, ARS, Beltsville, MD 20705, USA

HIGHLIGHTS

- >60% of the studied sites had a Cd content in cacao beans above the critical level.
- Bean Cd concentration was closely correlated with available Cd in soil.
- Soil Cd contamination is likely resulted from anthropogenic activities.
- Unlike other crops, Cd in cacao plant tissue changed as: beans > shell > > leaves.
- M3- or HCl-extractable Cd is adequate for estimating plant available Cd in soil.

GRAPHICAL ABSTRACT



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ABSTRACT

Cadmium (Cd) content in cacao beans above a critical level (0.6 mg kg^{-1}) has raised concerns in the consumption of cacao-based chocolate. Little is available regarding Cd concentration in soil and cacao in Ecuador. The aim of this study was to determine the status of Cd in both, soils and cacao plants, in southern Ecuador. Soil samples were collected from 19 farms at 0–5, 5–15, 15–30, and 30–50 cm depths, whereas plant samples were taken from four nearby trees. Total recoverable and extractable Cd were measured at the different soil depths. Total recoverable Cd ranged from 0.88 to 2.45 and 0.06 to 2.59, averaged 1.54 and 0.85 mg kg^{-1}, respectively in the surface and subsurface soils whereas the corresponding values for M3-extractable Cd were 0.08 to 1.27 and 0.02 to 0.33 with mean values of 0.40 and 0.10 mg kg^{-1}. Surface soil in all sampling sites had total recoverable Cd above the USEPA critical level for agricultural soils (0.43 mg kg^{-1}), indicating that Cd pollution occurs. Since both total recoverable and M3-extractable Cd significantly decreased depth wise, anthropogenic activities are more likely the source of contamination. Cadmium in cacao tissues decreased in the order of beans > shell> > leaves. Cadmium content in cacao beans ranged from 0.02 to 3.00, averaged 0.94 mg kg^{-1}, and 12 out of 19 sites had bean Cd content above the critical level. Bean Cd concentration was highly correlated with M3- or HCl-extractable Cd at both the 0–5 and 5–15 cm depths (r = 0.80 and 0.82 for M3, and r = 0.78 and 0.82 for HCl; $P < 0.01$). These results indicate that accumulation of Cd in surface layers results in excessive Cd in cacao beans and M3- or HCl-extractable Cd are suitable methods for predicting available Cd in the studied soils.

* Corresponding author.
E-mail address: zhe@ufl.edu (Z.L. He).

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1. Introduction

Cadmium (Cd) pollution poses a threat to food safety and human health in the world. Intake of excess Cd in contaminated food results in severe damage in organs such as lungs and liver, which eventually leads to the onset of cancer and other deadly disorders (Adriano, 2001; Kabata-Pendias, 2011). Cadmium has no metabolic function in plants but can accumulate in root, shoot and edible parts such as grains and cacao beans (*Theobroma cacao*, L.) (Zarcinas et al., 2004; Rascio and Navari-Izzo, 2011). Plants can tolerate Cd concentration at low levels without expressing any symptoms of toxicity, but accumulation of Cd in edible parts often causes adverse effects on human health (Baligar et al., 1998; Benavides, 2005; Marschner, 2012).

Plant absorbs Cd as divalent cation (Cd), which is the most predominant and mobile form of Cd in soil and the environment. In non-polluted soils, Cd concentrations range from 0.01 to 1.1 mg kg^{-1} with an average of 0.41 mg kg^{-1} (Singh and McLaughlin, 1999; Kabata-Pendias, 2011). Burt et al. (2003), following an extensive soil survey in the US, reported a mean of 0.40 mg kg^{-1}. In Florida, Ma et al. (1997) measured a geometric mean of 0.21 mg kg^{-1} for Cd, which is lower as compared to 0.38 mg kg^{-1} reported by Holmgren et al. (1993). The United States Environmental Protection Agency (USEPA) established a critical level of 0.43 mg^{-1} of total Cd in agricultural soils (USEPA, 2002). In western China, Zhang et al. (2002) estimated soil Cd concentrations of 0.01 mg kg^{-1} which is below China's average of 0.097 mg kg^{-1}. Additionally, Wang and Chen (1998) reported average values between 0.04 and 0.15 mg kg^{-1} in ten other regions of eastern China. In Brazil, Fadigas et al. (2006) obtained reference values for seven trace metals from representative tropical soil orders; the authors proposed a value of 0.5 mg kg^{-1} for total Cd. Higher concentrations of Cd have been reported in soils worldwide. These abnormal concentrations are due in part to weathering of parent materials, but more commonly, to anthropogenic activities (Adriano, 2001; Chaney, 2010; Kabata-Pendias, 2011). Unfortunately, neither reference values nor soil Cd levels are available for agricultural production systems in Ecuador.

Weathering of Cd rich sedimentary rocks is known to "naturally" raise Cd concentration in soils. Concentrations of Cd in some sedimentary rocks decrease in the order: marlstone (2.6 mg kg^{-1}) > bentonite (1.4 mg kg^{-1}) > bituminous shale (0.80 mg kg^{-1}) (Singh and McLaughlin, 1999). Garrett et al. (2008) reported one of the highest values for soil-Cd due to weathering of phosporite in Jamaica; this group measured a concentration as high as 200 mg kg^{-1} of total Cd in those bauxitic soils.

Despite natural build-up of Cd in soils, artificial contamination is by far the greatest concern in heavy metal biogeochemistry. Application of phosphate fertilizers is considered one of the major inputs of Cd in agricultural soils, due to elevated Cd concentration in phosphate fertilizers, which could be as high as 130 mg kg^{-1} (Khwaja et al., 1997; Chen et al., 2007; Jiao et al., 2012). Disposal/utilization of wastes including wastewater, manures, compost and/or sewage sludge has been reported to increase levels of Cd in soils. Cadmium concentrations in compost and sludge vary from 0 to 16 mg kg^{-1}, depending on the raw material and technology employed to produce the organic amendments (Smith, 2009; Kabata-Pendias, 2011; Alloway, 2013). The application of fertilizers and/or soil amendments is not a common practice on cacao farms; instead, the input of nutrients depends mainly upon the decomposition of litter and residues from harvest (Hartemink, 2005). Other sources of Cd in soils are: zinc (Zn) and lead (Pb) mining, steel and battery production, plating, and smelting, etc. (García et al., 2001; Chaney, 2010).

For crop management and environmental purposes, the distinction between geogenic and anthropogenic contamination is imperative. One of the most common practices is to determine the vertical distribution of the metal along an undisturbed soil profile. Higher concentration of Cd in the parent materials than the overlying soil layers may suggest a likely geological source of contamination (García et al., 2001; Caridad-Cancela et al., 2005; Buccolieri et al., 2010), whereas anthropogenic contamination may be the case if the opposite is true (Caridad-Cancela et al., 2005). Sources of soil contamination can be also determined by historical changes of Cd concentrations along soil profile as affected by time and human activities (McDowell et al., 2013). This approach requires reliable historical data, which are often difficult to obtain.

The discrimination between geogenic and anthropogenic sources is important for the management of contaminated soils. However, the assessment of bioavailable pool (s) of metals in soils is more relevant from biological perspective (Adriano, 2001). Furthermore, total concentration may not indicate bioavailability of Cd in soils as available Cd accounts for only a small portion of its total. In addition, many soil and plant factors can influence the labile pools of Cd (Degryse et al., 2003; Caridad-Cancela et al., 2005; Kirkham, 2006). In soils, metal bioavailability is controlled by several factors such as total metal content, pH, soil organic matter (SOM), cation exchange capacity (CEC), and clay content (He et al., 2005; Kirkham, 2006; Alloway, 2013). Several techniques have been developed to estimate bioavailable Cd in soils. They include chemical extraction with single or a series of reagents. The preference of one method over others is often determined by the correlation between extractable metal in soil and the corresponding plant uptake (Amacher, 1996; Rauret, 1998; Degryse et al., 2003; Zhang et al., 2010). Different reagents, from neutral salts to strong acids have been applied to estimate available Cd in soil (Zhang et al., 2006). NH_4OAc and $CaCl_2$ are neutral salts with a low extraction power, but their estimation usually yields a significant correlation with plant uptake of Cd, whereas strong acidic reagents, such as HCl, Mehlich 3 (M3) and Mehlich 1 (M1), or chelates like EDTA and DTPA-ETA, have a greater extracting ability but they are often poorer indicators of Cd availability in soils (Menzies et al., 2007; Zhang et al., 2010). However, Fontes et al. (2008) reported a significant correlation between Cd concentration in dry bean (*Phaseolus vulgaris*) or lettuce (*Lactuca sativa*) and M3 extractable Cd in three highly weathered soils in Brazil.

Cacao (*T. cacao*, L.) is one of the most economically important commodities in Ecuador, with a cultivated area of 434,000 hectares (ha) across the country (INEC, 2012). Guayas and El Oro provinces are characterized for agricultural as well as mining activities, particularly artisanal gold mining, which has contributed to heavy metal contamination in rivers (Bech et al., 1997; Mounicou et al., 2003; Ramirez Requelme et al., 2003). In a recent study, the concentration of heavy metals in sediment and water of three rivers in southern Ecuador were monitored, and two of the three rivers were reported to have Cd concentrations higher than USEPA maximum contaminant level (MCL), whereas sediments from one river contained Cd levels above Environmental Canada Probable Effect (Carling et al., 2013). Water from these rivers has been utilized to irrigate cacao fields for numerous years in the studied area.

Cacao produced in Ecuador and other South America countries has favorable quality for making fine chocolate (Loor et al., 2009). However, concentrations of heavy metals (including Cd and Pb) above a critical level (0.6 mg kg^{-1} for Cd), established by European Union, has raised concerns of safety in the consumption of cacao-based chocolate (dark chocolate) (Mounicou et al., 2003; Zarcinas et al., 2004; Dahiya et al., 2005). For instance, cacao-based chocolate contained 3.4 times more Cd than milk-based chocolate (Dahiya et al., 2005). Therefore, Cd contamination has impacted the production of cacao and subsequently chocolate worldwide.

Limited information is available regarding Cd concentration in raw cacao beans in South America. Higher levels of Cd were reported in cacao powder from Ecuador, Venezuela and Malaysia, as compared to those from Brazil and African countries (Mounicou et al., 2003). In Peninsular Malaysia, Zarcinas et al. (2004) registered cacao with the highest concentration of Cd. Unfortunately, no information is available regarding Cd concentration in soil, cacao plant, and cacao bean in Ecuador. This information is critical for developing management solutions to the contamination of cacao bean by Cd.

The objectives of this study were to: i) investigate the status of Cd in soils of representative cacao farms in Ecuador and its relationship with