Chemical speciation of cadmium: An approach to evaluate plant-available cadmium in Ecuadorian soils under cacao production

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HIGHLIGHTS

- Soil Cd fractionation was performed to identify available Cd pools.
- Oxidizable and acid soluble Cd account for >60% of total recoverable Cd.
- Acid-soluble Cd is correlated with extractable soil Cd, or cacao bean Cd.

ARTICLE INFO

ABSTRACT

Elevated concentration of cadmium (Cd) in cacao beans has raised serious concerns about the chocolate consumption on human health. Accumulation of Cd in cacao bean in southern Ecuador has been related to soil contamination. In this study, soil fractionation approach was used to identify available Cd pools in the soils and to correlate these Cd pools with bean Cd concentration and soil test indexes. The distribution of soil Cd fractions decreased in the order: oxidizable > acid-soluble > residual > reducible >> water-soluble (+exchangeable). Oxidizable and acid-soluble fractions accounted for 59 and 68% of the total recoverable Cd for the 0–5 and 5–15 cm soil depth, respectively. Acid-soluble fraction was closely related to bean-Cd, with correlation coefficients (r) of 0.70 and 0.81 ($P < 0.01$) for the 0–5 and 5–15 cm soil depth, respectively. Acid-soluble Cd was significantly correlated with 0.01 M HCl- (r = 0.99, $P < 0.01$) or Mehlich 3- extractable Cd (r = 0.97, $P < 0.01$). These results indicate that acid-soluble Cd fraction is an important part of available Cd pool. Since approximately 60% of Cd in the cacao-growing soils is related to the acid-soluble fraction and bound to organic matter, remediation of the contaminated soils should consider to the dynamics of soil pH and organic matter content.

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1. Introduction

Cadmium (Cd) is one of the most plant-available elements in agricultural soils, minimal alterations in soils conditions greatly affect its mobility and availability (Kabata-Pendias, 2011). Therefore, this metal readily enters food chains through daily-consumed grains, vegetables, or sweets such as chocolate (Zarcinas et al., 2004; Yu et al., 2006; Liu et al., 2007). Determination of plant available Cd, rather than total content, is more meaningful when assessing deleterious effects of Cd-contaminated soils (Adriano, 2001). To address this issue, various techniques have been developed over the years, among these, chemical analysis, such as sequential and single extraction procedures, have been successfully applied to identify available pools of Cd in a reliable and cost-efficient manner (Meers et al., 2007; Bacon and Davidson, 2008; Rao et al., 2008).

Sequential and single extraction methods have been broadly used in a range of soils and sediments to identify various pools of

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metals, such as Cd (Amacher, 1996; Buccolieri et al., 2010). A variety of sequential extraction schemes have been proposed, validated, and adopted in different countries and/or regions to evaluate readily and potentially bioavailable metals in soils (Rauret, 1998; Bacon and Davidson, 2008). Depending on the reagents used, sequential extraction analysis divides total metal content into distinctive operational pools by applying a series of reagents to the same sample in a chronological order, the extraction capacity increases through each advancing step in the procedure (Tessier et al., 1979; Rauret, 1998; Gleyzes et al., 2002; Bacon and Davidson, 2008; Rao et al., 2008). Single extraction is the removal of metals from soil through one or a mix of reagents in one step. These could vary from neutral salts to strong acids, and the strength of the reagent, and the conditions of the extraction. All of the above determine the capacity of the method in dissolving the element in soils.

Soluble fractions, such as water soluble, exchangeable, and acid soluble, are usually related to plant-available Cd (Kashem et al., 2007; Rao et al., 2008; Kosolsaksakul et al., 2014; Sungur et al., 2014). Normally, when Cd is artificially introduced in soil a high percentage is recovered from soluble fractions, whereas if Cd is inherited from parent materials, it is more likely found in the residual fraction (Rao et al., 2008; Nogueira et al., 2010; Aikpokpodion et al., 2012). Commonly, the extraction of soil Cd by neutral salts, such as $CaCl_2$, NH_4OAc and NH_4NO_3 are reported as good indicators of plant-available Cd (Degryse et al., 2003; Meers et al., 2007; Zhu et al., 2012). Correlation (s) between fractionation and available Cd estimated by validated extractable methods may aid in understanding the association of plant-available Cd and soil constituents (Bacon and Davidson, 2008).

Fractionation of soil Cd has been conducted for a variety of soils; however, scant information is available regarding Cd pools in cacao growing soils, particularly in Ecuador. These soils are characterized by the accumulation of soil organic matter (SOM) in top layers; mainly due to decomposition of litter, woody tissues from pruning, dead roots, and harvest residues, which alter the cycling of elements and retention capacity of soils (Beer, 1988; Wood and Lass, 2008). To identify available pools of soil-Cd in cacao plantations from Nigeria, Aikpokpodion et al. (2012) partitioned soil Cd into six operational pools: water soluble, exchangeable, carbonate-bound, Mn–Fe oxides-bound, and organic-bound Cd. They reported that residual fraction, determined by HNO_3 digestion, was the main pool of Cd in those soils, which is not available to plant (Aikpokpodion et al., 2012). Except for copper, heavy metals in Nigerian soils are mainly derived from weathering of parent material (Aikpokpodion, 2010).

Cacao (*Theobroma cacao*, L.), with nearly 500,000 ha, is the most planted crop in Ecuador and is therefore an important agricultural commodity for the economy. A special characteristic of Ecuadorian cacao is its special flavor and aroma, which adds a great appreciation and fetch high value in the chocolate industry (Afoakwa et al., 2008). The presence of Cd in cacao beans greatly affects the quality and safety if Cd is transferred along with chocolate production chain. In a previous study, cacao beans from southern Ecuador (Guayas and El Oro provinces) were reported to have excessive levels of Cd (based on European Union standards); furthermore, this high bean Cd concentration was significantly correlated to soil-Cd, particularly, to Mehlich 3 (M3) and 0.1 M HCl extractable Cd (Chavez et al., 2015). Additionally, Cd was mostly accumulated in beans, rather than leaves or bean-coating (Chavez et al., 2015). To control the intake of Cd-contaminated chocolate, the European Union established a threshold for Cd in cacao beans (and other byproducts) of 0.6 mg kg^{-1} (ICCO, 2012). This measure will initiate in 2019 and will affect Ecuadorian exports if bean Cd concentration does not meet the standard.

In order to fully establish the connection between soil and bean Cd concentration, a soil fractionation analysis was conducted with the following objectives: i) to determine the various pools of extractable Cd in soils at two depths in 15 cacao production sites in southern Ecuador, ii) to analyze the interrelationships between soil Cd pools and Cd concentration in cacao beans, and, iii) to correlate extractable Cd with soil Cd pools (fractions), for establishing reliable soil tests for predicting Cd availability in soils.

2. Materials and methods

Soil and plant samples were collected from small-scale cacao farms (<5 ha) located in southern Ecuador (Guayas and El Oro provinces). Samples were collected at fifteen sites, at each site; a composite soil sample was obtained from four equidistant sampling points. In a previous study, Chavez et al. (2015) determined that Cd in cacao-growing soil was highly accumulated within the first 15 cm of soil profiles. Therefore, to contrast Cd pools at different depths, samples were taken at the 0–5 and 5–15 cm depth from the surface.

Negligible concentration of Cd was reported on leaves or bean-coatings, henceforth; only cacao beans were analyzed in this study (Chavez et al., 2015). These beans were collected from three to four mature cacao pods from trees adjacent to soil samples.

2.1. Geochemical analysis

Basic soil properties were analyzed as follows: pH and electrical conductivity (EC) were measured in deionized water (1:2 soil/water ratio) using a pH/ion/conductivity meter (Denver Instrument, Co.); total carbon (C) was determined by a combustion method with a C/N analyzer (Vario MAX CN Macro Elemental Analyzer, Hanau, Germany) (Sparks et al., 1996).

Total recoverable (TR) Cd was determined according to USEPA method 3050B (USEPA, 1996). Two single extraction methods were applied to the soil samples, Mehlich 3 (M3) and 0.1 M HCl (HCl) (Amacher, 1996). Detailed procedures and results of total recoverable and extractable Cd were presented in Chavez et al. (2015).

Soil Cd was fractionated into five operational pools according to the scheme of Tessier et al. (1979) with two replicates. In summary, Cd pools were extracted as follows: (1) water soluble and exchangeable: 20 mL of 0.1 M $Mg(NO_3)_2$; (2) acid-soluble (carbonate bound): 20 mL of 1 M NaOAc (pH 5); (3) reducible: 40 mL of 0.2 M ammonium oxalate + 0.2 M oxalic acid, and 0.1 M ascorbic acid (pH 3), (4) oxidizable: 25 mL of 30% H_2O_2 (pH 2) + 3.2 M NH_4OAc, and (5) the residual fraction was obtained by the difference between the sum of the preceding fractions and the total recoverable Cd. After each extraction, samples were washed three times with 5 mL of ethanol, and allowed to dry completely before next extractions (Tessier et al., 1979; Amacher, 1996). Digestion solution and soil extracts were analyzed from three replicates using inductively coupled plasma optical emission spectrometry (ICP-OES, Ultima, JY Horiba Group, NJ, USA).

2.2. Cd concentration in cacao bean

Prior to analysis, cacao beans were ground to powder in an agate mortar, 0.4 g of ground cacao beans were digested, in an open system, with 6 mL of concentrated nitric acid (HNO_3) at 80 °C and 140 °C each for 180 min, three replicates were digested per sample. Once a clear solution was attained, digestates were diluted to 25 mL with nano-pure water and filtered through a 0.45 μm membrane filter before analysis of Cd.

Cadmium in plant digests was determined using the ICP-OES.