Presence of heavy metals in organic cacao (*Theobroma* cacao L.) crop

Presencia de metales pesados en cultivo de cacao (*Theobroma cacao* L.) orgánico

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Abstract

The presence of heavy metals in cocoas crop is becoming a problem for farmers and cooperatives at Huánuco and Ucayali regions, Peru. In this research cadmium and lead contents in cocoa soils and leaves were evaluated. For it, soil and foliar samples were collected in 22 organic crop plots located at Huánuco (17) and Ucayali (5) regions. Pearson correlation analysis was performed between available content of lead and cadmium in soils with foliar variables (P, Mg, Ca, Zn, Cd, Pb) and soil (Sand, Clay and K) variables. According to the soil analysis only the potassium was deficient; while in leaf tissue deficiencies of N, P, K, Mg and Zn were observed. The average values of available cadmium and lead in soils were 0.53 ppm and 3.02 ppm and in leaves were 0.21 ppm and 0.58 ppm respectively.

Key words: Cadmium, contaminants, heavy metals, lead, soil, *Theobroma cacao*.

Resumen

La presencia de metales pesados en el cultivo de cacao (*Theobroma cacao* L.) es actualmente un grave problema para agricultores y cooperativas de las regiones Huánuco y Ucayali, Perú. En el presente trabajo se evaluaron los contenidos de cadmio y plomo en suelos y hojas del cacao en estas regiones. Para el efecto se recolectaron y analizaron en laboratorio muestras tomadas en 22 parcelas con cultivos orgánicos de esta especie, 17 en la región Huánuco y cinco en la región Ucayali. Se realizaron análisis de correlación de Pearson entre los contenidos de plomo y cadmio disponibles en el suelo con variables foliares (P, Mg, Ca, Zn, Cd, Pb) y del suelo (arena, arcilla y K). En los suelos, sólo en el caso de potasio se presentan deficiencias; mientras que en el tejido foliar se presentaron deficiencias de N, P, K, Mg y Zn. Los valores promedio de cadmio y plomo disponible en los suelos fueron 0.53 y 3.02 ppm y en las hojas de cacao de 0.21 y 0.58 ppm respectivamente.

Palabras clave: Cadmio, contaminantes, metales pesados, plomo, suelo, *Theobroma cacao*.

Introduction

Organically cultivated cacao (*Theobroma cacao* L.) is one of the main socio-economic activities in the Huánuco and Ucayali regions in Perú. The largest markets are the European (France, England, Belgium) and the United States. Cadmium and lead are found naturally on the earth crust as minerals that can be absorbed by plants and from them can be taken by humans, which constitutes a potential health risk (Prieto *et al.*, 2009). Cacao plants absorb heavy metals from soils and concentrate them in seeds (Augstburger *et al.*, 2000). Evaluation of cadmium content in cacao seeds in plots of these regions revealed the presence of cadmium at higher levels than allowed (0.5 ppm) (Cárdena, 2012), that can limit export of this agricultural product. In this context, the present research aimed at the determination of available cadmium and lead contents in soil and leaves of organic cacao.

Materials and methods

The research was performed in 22 plots of seven years old organic cacao that was in production, 17 were located in Huánuco region (75° 49' W, 09° 09' S) and five were in the Ucayali region (75° 12' W, 08° 49' S), Perú. Soil samples were taken in December, 2010 and were used for physical and chemical analysis. In each plot 20 subsamples were taken and mixed to get 1 kg sample that was sent to the lab for the following analysis: texture by the Bouyoucus hydrometer method (1962), pH (1:1), organic matter (OM) by the Walkey and Black method (1934), available P by the modified Olsen method (1954), available potassium using 6N sulfuric acid (Cano *et al.*, 1984), CEC (cation exchange capacity) according to the 1N ammonium acetate pH 7 (Rhoades, 1982), interchangeable calcium, magnesium, potassium and sodium by extraction with ammonium acetate and reading on an atomic absorption spectrophotometer (Jackson, 1964), effective CEC by 1N KCl displacement (Díaz and Hunter, 1978), aluminum and hydrogen by Yuan method (1958), available cadmium and lead using extraction by 0.05M EDTA pH 7 (Westerman, 1990).

For leaf analysis, two leaves of randomly selected plants were collected in each plot for a total of 20 leaves. This material was placed on labelled bags and sent to the lab where it was dried and grinded for nitrogen (N) analysis by the Kjendahl method, phosphorus (P) by the Metavanadate and cation method, and read on an atomic absorption spectrophotometer (AOAC, 1995).

Obtained data were processed by the statistical software SPSS 12 (2003) to perform Pearson correlation analysis between available cadmium and lead contents in soil and leaf (P, K, Mg, Ca, Zn, Cd, Pb) and soil variables (sand, clay and K).

Results and discussion

Nutrient content in soil and leaf tissue

According to the IPNI (2011) recommendations, soils had suitable chemical properties for cacao crop (Table 1). However, K_2O content was low in some plots that presented lower levels than the ones recommended for cacao growth (>300 kg/ha). Aluminum saturation percentage is within the allowed levels for the crop (< 30%), except for soils on the location H-13, where it was 32%.

Leaf analysis showed deficiencies in N, P, K, Mg and Zn contents (Table 2), according to the recommendations of Aikpokpodion (2010) for this crop. In the case of K the low levels are associated with the low levels of this nutrient in the soil.

Heavy metals content in soil and leaves

In soil, the average contents of available cadmium and lead were, respectively, 0.53 ppm and 3.02 ppm (Table 3). The European Union establishes that in agricultural soils the maximum concentration of heavy metals in total is 3 ppm for cadmium and 300 ppm for lead (Acevedo, 2005). Reyes and Maria (2004) found in organic cacao crops in Dominican Republic that available cadmium and lead in soils represent 33% and 11.7% of the total cadmium and lead in the plant, respectively.

Heavy metals are present in soils as natural components or as a consequence of antropogenic activities (Prieto *et al.*, 2009). In the zones of study has not been determined the

Table 1. Physico-chemical analysis of soils in this study.

Location	Texture	pH	OM (%)	P (ppm)	K_2O (kg/ha)	CEC. cmol(+)/kg	Al sat. (%)
H-1	Clay loam	5.26	2.09	8.6	278	9.65	6.22
H-2	Loam	7.53	2.30	8.6	398	11.20	0
H-3	Loam	7.17	2.72	9.8	537	10.84	0
H-4	Sandy loam	7.29	2.09	9.6	340	10.60	0
H-5	Sandy loam	7.23	2.09	10.3	438	9.71	0
H-6	Silty loam	7.19	2.51	9.4	554	10.20	0
H-7	Loam	6.67	2.93	8.4	263	11.04	0
H-8	Sandy loam	6.38	3.97	9.1	606	9.04	0
H-9	Sandy clau loam	5.26	2.90	10.4	206	9.70	6.19
H-10	Loam	6.88	2.93	11.5	541	10.47	0
H-11	Loam	4.68	2.72	6.9	558	7.26	13.77
H-12	Loam	7.14	2.72	8*6	632	10.24	0
H-13	Loam	4.03	2.51	9.4	494	4.38	31.96
H-14	clay loam	5.41	3.34	12.2	134	9.58	5.22
H-15	Loam	5.08	2.72	9.9	190	8.57	15.17
H-16	Clay loam	6.72	2.72	10.2	348	10.54	0
H-17	Sandy loam	6.99	1.04	11	548	9.78	0
U-1	Sandy clay loam	4.88	2.30	12.4	257	9.73	16.44
U-2	Sandy clay loam	5	2.09	7.9	344	9.22	2.71
U-3	Sandy clay loam	4.73	2.72	10.6	221	7.31	4.10
U-4	Clay loam	5.18	2.09	10.9	369	7.16	3.49
U-5	Clay loam	5.6	3.34	12.8	265	6.52	0
μ		6.05	2.58	9.93	387.31	9.22	4.79
S.D.		1.07	0.58	1.47	147.63	1.67	7.83

μ: average; S.D: standard deviation.

origin of these metals on soil. Cárdenas (2012) found in plots with organic crops in the Huánuco region that the highest levels of available cadmium in soil (1.82 and 1.63 ppm) were presented at the bank of Huallaga and Tulumayo rivers, respectively. Walsh, cited by Cárdenas (2012), observed cadmium presence in sediments of the Huallaga river, being higher on the dry season (may-august) with values between 1.28 and 2.57 ppm.

In the leaf tissue were found average values of 0.21 ppm for cadmium and 0.58 ppm for lead. Kabata-Pendias (2000) considered that in mature leaves the maximum tolerable concentration of heavy metals is 0.5 ppm for cadmium and 10 ppm for lead, values that are higher than the ones found in this experiment. Izquierdo (1998) found in cacao leaves in Barlovento, Venezuela, values of cadmium between 0 and 21 ppm, suggesting high variability of this element.

Heavy metals correlations

In Table 4 are shown the values for Pearson correlations of available cadmium and lead in soil with the variables evaluated in soil and cacao leaves. This correlation was significant and positive ($P < 0.05$) between total cadmium in leaf tissue and available cadmium in soil; contrary, the correlation between cadmium in soil and leaf content of calcium and magnesium was significant but negative. One explanation for these results is that the available form of these elements in soil is the ionic form $^{+}2$, which means that there is a possible competition between these three elements for the absorption places in the root of the plant, affecting the Mg level in the leaves to levels below the reference. Cadmium is not an essential element for plants, therefore, it is assumed that there are not specific absorption mechanisms. Among the responsible proteins for cadmium entrance to the cell is highlighted the calcium specific transporter LCT1 and the IRT1 protein that belongs to the zinc and iron family of transporters Rodríguez-Serrano *et al.*, 2008). Benavides *et al.* (2005) consider that cadmium absorption at the root level is in direct competition with other nutrients such as calcium, potassium, magnesium, iron, copper, manganese, zinc, because they can be absorbed by the same carrier proteins.

Correlation between available cadmium content in the soil and sand percentage in soil was negative ($P < 0.05$). If it is consider that the average soil texture in this study has a trend from loam to clay loam, it can be inferred that these kinds of textures favor a

Table 2. Nutrient content on leaf samples of cacao plants in this study.

Location	N	P	K	Ca	Mg	Fe	Mn	Zn	Cu
			(%)				ppm		
H-1	1.29	0.21	1.16	1.67	0.36	86.33	91.33	39.36	9.43
H-2	2.18	0.16	1.17	2.53	0.37	104.33	21.95	40.74	7.44
H-3	1.08	0.14	1.16	2.30	0.36	51.44	31.79	29.83	9.33
H-4	1.38	0.17	1.15	2.69	P*38	175.50	41.10	36.08	8.43
H-5	1.74	0.18	1.16	2.64	0.37	134.98	39.25	34.49	13.11
H-6	1.76	0.17	1.15	2.43	0.38	109.56	17.08	41.84	9.80
H-7	1.46	0.14	1.16	2.48	0.38	161.12	151.92	36.89	8.03
H-8	1.01	0.13	1.14	2.73	0.39	147.38	76.58	40.90	5.50
H-9	1.69	0.16	1.15	2.43	0.38	93.73	244.58	36.29	8.66
H-10	0.98	0.19	1.16	2.49	0.38	73.80	55.88	44.28	8.95
H-11	1.51	0.14	1.16	2.37	0.38	92.34	239.63	40.45	9.48
H-12	1.55	0.12	1.15	2.64	0.38	70.8	58.94	44.33	6.98
H-13	1.85	0.17	1.15	1.40	0.36	279.36	122.04	30.84	8.52
H-14	1.66	0.20	1.16	2.04	0.37	254.90	144.75	39.25	10.45
H-15	1.89	0.09	1.15	2.50	0.37	110.59	264.63	40.41	5.39
H-16	1.81	0.23	1.17	2.17	0.37	253.05	41.78	35.15	10.35
H-17	1.34	0.15	1.16	2.58	0.37	258.73	60.42	34.78	10.15
U-1	1.23	0.17	1.14	2.20	0.37	106.31	128.23	32.82	8.20
U-2	1.71	0.16	1.14	2.45	0.37	84.85	156.24	35.55	7.41
U-3	1.77	0.13	1.14	2.39	0.38	86.63	171.80	37.82	6.82
U-4	1.74	0.2	1.16	2.45	0.37	73.12	115.66	33.29	8.12
U-5	2.35	0.19	1.15	2.34	0.38	106.40	125.43	39.43	9.30
µ	1.59	0.16	1.15	2.36	0.37	132.51	109.14	37.49	8.63
S.D.	0.35	0.03	0.01	0.32	0.01	69.02	73.95	3.98	1.72

µ: average; S.D.: standard deviation.

Table 3. Values (ppm) of heavy metals in soil and leaf tissue of cacao.

Location	Soil		Leaves		Location	Soil		Leaves	
	Cd	Pb	Cd	Pb		Cd	Pb	Cd	Pb
H-1	1.52	1.87	0.33	0.49	H-13	0.53	1.07	0.18	0.59
H-2	0.47	2.21	0.19	0.59	H-14	0.44	3.17	0.19	0.59
H-3	0.48	1.95	0.18	0.64	H-15	0.42	1.73	0.21	0.57
H-4	0.37	1.81	0.18	0.64	H-16	0.93	2.08	0.26	0.58
H-5	0.51	4.27	0.17	0.56	H-17	0.50	2.03	0.19	0.60
H-6	0.53	5.71	0.20	0.57	U-1	0.43	2.85	0.20	0.52
H-7	0.42	3.33	0.21	0.54	U-2	0.44	2.77	0.20	0.54
H-8	0.49	4.27	0.21	0.59	U-3	0.46	4.19	0.18	0.54
H-9	0.38	2.16	0.30	0.53	U-4	0.44	2.56	0.19	0.58
H-10	0.39	5.92	0.19	0.57	U-5	0.59	1.89	0.17	0.59
H-11	0.31	1.71	0.19	0.63	µ	0.53	3.02	0.21	0.58
H-12	0.54	6.83	0.22	0.60	D.E.	0.25	1.55	0.04	0.04

µ: average; S.D.: standard deviation.

Table 4. Analysis of Pearson correlation between available cadmium and lead in soil with leaf variables (f) and some soil properties.

Element	P-f	Mg-f	Ca-f	Zn-f	Cd-f	Pb-f	Sand	Clay	K-s
Cd-s	0.483*	-0.425*	-0.522*	0.032	0.441*	-0.437*	-0.429*	0.307	-0.114
Pb-s	-0.138	0.507*	0.420	0.583*	-0.365	-0.106	0.084	-0.445*	0.449*

N = 22, * significant correlation (P < 0.05), ** highly significant correlation (P < 0.01).

higher presence of available cadmium absorbed in the soil matrix, in this case to the clay. Estévez *et al.* (2000) evaluated the retention and mobility of cadmium and zinc in three soils of Galicia, Spain, and found higher retention in soil with high content of O.M., clay, effective CEC and lower aluminum percentage saturation. Holmgren *et al.* (1993) consider that cadmium varies with soil evolution, with lower values on more evolved soils, of acid pH, low CEC values and sandy texture.

For the case of lead, there was a negative correlation (P < 0.05) between this element available in soil and the presence of clay, indicating that this mineral in the soil affects lead availability. Garrido *et al.* (2008) evaluated the behavior of cadmium and lead on acid soils in laboratory conditions and found a high retention of the last one, in contrast to the high mobility of the first one. Illera *et al.*, (2004) found that lead is retained at the edges of kaolinite, a common clay in the humid tropical zones, like the ones of this experiment. A positive correlation (P < 0.05) was observed as well between lead on soil and leaf content of Mg and Zn and with potassium in soil.

Conclusions

- Soils in this study have suitable physical and chemical conditions for cacao crop, except on the H-14 and H-15 locations, where there is a low level of K_2O.
- In leaf tissue of cacao were observed deficiencies of N, P, K, Mg and Zn.
- The average values of Cadmium and Lead (0.53 and 3.02 ppm, respectively) in these soils can be considered as low.
- There were correlations of cadmium in the soil and leaf content of P, Mg, Ca, and Pb; and of lead in the soil with leaf content of Mg, Zn and K and clay in the soil.

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