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Rethinking the proportionality of cadmium limits in raw unprocessed cocoa beans

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Abstract

Cadmium (Cd) tends to bioaccumulate in cocoa (*Theobroma cacao* L.) grains, affecting human health and marketing potential. The European Union (EU) drafted and approved in 2019 the Regulation Nº. 488/2014 for processed cocoa, and led to research on bioaccumulation in grains, potential health risks, product quality, and export potential. The results show high Cd levels in cocoa at different regions in the Latin American**.** However, this regulation does not stipulate maximum limits for unprocessed cocoa. In this absence, the regulations have used these parameters as a reference to the limits in processed cocoa, generating over estimation of metal concentration, market disputes and trade distortion. This article reviews the levels of Cd in cocoa almonds, justifies the inappropriate implementation of this regulation to unprocessed cocoa, and makes proposals for maximum limits in almonds and their implications. The present model provides adequate categorization and showing that the maximum limits Cd for row almonds of 1.14 μg g^{-1}, 1.22 μg g^{-1} and 1.02 μg g^{-1} are significantly reduced from the values categorized as high (according to EU), from 70.59 to only 30.53 %, a reasonable figure which is appropriate for the unprocessed cocoa. Analysis of seed fractions, and primary products show where is the variability in Cd concentrations.

Key words: bioaccumulation; cadmium; cocoa; EU Regulation Nº. 488/2014; *Theobroma cacao*.

Replanteamiento de la proporcionalidad en los límites del cadmio en el grano de cacao crudo seco sin procesar

Resumen

El cadmio (Cd) se bioacumula en los granos de cacao (*Theobroma cacao* L.), afectando la salud humana y el potencial de comercialización. La Unión Europea (UE) aprobó en 2019 el Reglamento No. 488/2014 para el cacao procesado, y dio lugar a investigaciones sobre la bioacumulación en los granos, los riesgos potenciales para la salud, la calidad del producto y el potencial de exportación. Resultados muestran altos niveles de Cd en cacao de diferentes regiones de América Latina. Este reglamento no establece límites máximos para el cacao sin transformar. Utilizando estos parámetros como referencia a los límites del cacao procesado, ocurre una sobreestimación de la concentración de metales, disputas y distorsión comercial. Aquí se examinan niveles de Cd en almendras de cacao, se justifica el inadecuado uso del reglamento y se proponen máximos para almendras y sus consecuencias. Esto proporciona una nueva categorización a los límites máximos Cd para las almendras de 1,14 μg g^{-1}, 1,22 μg g^{-1} y 1,02 μg g^{-1} reduciendo significativamente los valores (según la UE), de 70,59 a sólo 30,53 %; una cifra razonable y adecuada para el cacao no transformado. Los análisis de las fracciones de semillas y de productos primarios muestran dónde está la variabilidad en las concentraciones de Cd.

Palabras clave: bioacumulación; cadmio; *Theobroma cacao*, UE Regulación Nº. 488/2014.

Reavaliação da proporcionalidade dos Limites de Cádmio em grãos de cacau Crus, secos e não processados

Resumo

O cádmio (Cd) bioacumula-se nos grãos de cacau (*Theobroma cacao* L.), impactando a saúde humana e o potencial de mercado. Em 2019, a União Europeia (UE) adotou o Regulamento nº 488/2014 para o cacau processado, o que motivou pesquisas sobre bioacumulação nos grãos, potenciais riscos à saúde, qualidade do produto e potencial de exportação. Os resultados mostram altos níveis de Cd no cacau de diferentes regiões da América Latina. Este regulamento não estabelece limites máximos para o cacau não processado. O uso desses parâmetros como referência para os limites no cacau processado leva a uma superestimação das concentrações do metal, disputas e distorções comerciais. Este artigo examina os níveis de Cd nos grãos de cacau, justifica o uso inadequado do regulamento e propõe limites máximos para os grãos e suas consequências. Isso proporciona uma nova categorização dos limites máximos de cádmio para amêndoas: 1,14 μg g^{-1}, 1,22 μg g^{-1} e 1,02 μg g^{-1}, reduzindo significativamente os valores (de acordo com a UE) de 70,59 % para apenas 30,53 %, um valor razoável e adequado para cacau não processado. Análises das frações de sementes e produtos primários mostram onde reside a variabilidade nas concentrações de cádmio.

Palavras-chave: bioacumulação; cádmio; Regulamento da UE N.º 488/2014; *Theobroma cacao.*

Introduction

Many animal and plant species accumulate heavy metals, and therefore a number of regulations have been created that set the maximum permitted limits in the food industry. This accumulation is often "natural" by certain plant species called "accumulators or bioaccumulators" (Khan *et al.*, 2015). The causes may be of geophysical origin (weathering, volcanic eruptions), anthropogenic (industrialization, water pollution, fertilization, inappropriate agricultural practices), and others.

There is abundant evidence that cadmium causes a number of disorders in human health, as a result of its high mobility and bioaccumulative power (Reyes *et al*., 2016; Antoine, *et al*., 2017, Engbersen *et al*., 2019; Zug *et al.,* 2019, Maddela *et al*., 2020). As a result, studies have been carried out to determine the concentration of Cd in cocoa, trying to find and minimize the causes of this bioaccumulation, and thus seek alternatives in terms of cultivation areas, soil type, water sources, approaches to industrialized centers, and the indiscriminate use of chemical fertilizers (He *et al*., 2015).

To help maintain the quality of the product for the final consumer, avoid market distortions and mainly stimulate and protect the cocoa producer in the South American region (Perú, Ecuador, Brazil, Colombia and Venezuela) as the principals exporter countries, it is necessary to know the quality of the product to be exported. Soil cadmium pollution, and other metals, resulting from diverse sources, has posed an increasing challenge to soil quality and food security as well as to human health and a problem to be solved in the human foods. The European region is the main consumer of cocoa products and therefore the main trading partner for cocoa-exporting countries, particularly Latin American producer countries. This is why the European Union (EU) has established a regulatory standard for the concentration of cadmium in cocoa, since the population of this continent is the largest consumer almost tripling the global consumption standard, and because cadmium is a toxic element for health. The considerations made have a significant impact on the cocoa market of Latin American countries, where production comes from small producers, as opposed to West African production, which accounts for 66 % of the world total (Meter *et al*., 2019).

The implementation of Regulation No. 488/2014 which set tolerable limits between 0.1 to 0.8 $\mu g\ g^{-1}$ for cocoa products led researchers and producers to look for ways to reduce and adjust concentrations, to the limits set by the EU. However, research shows that soils generally have low concentrations of Cd, and the bioavailability of this metal to plants depends on soil-specific factors such as soil texture, the origin of irrigation water, of runoff, pH, among others possible. On the other hand, higher concentrations of Cd have been reported in the soil itself, this probably being caused by various factors between the soil-cocoa system. For example, fertilization with phosphate products is the main source of incorporation of Cd in the soil, and erroneous agricultural practices such as their use of fruit remains as fertilizer at the feet of plants. This is why the concentration values of Cd of ten exceed the limits set by the EU. The accumulation of fruit remains, exocarp, at the base of trees helps to increase the build-up of Cd and other metals. Another important factor is to avoid irrigation with industrial waste water, or that rainwater run-off does not come from such places and proximity from roads.

As mentioned above this regulation assigns a high value to chocolates (elaborated product) with total dry matter percentage 50 %, establishes tolerable limits for Cd in chocolate (final consumption), but uses arguments from the Environmental Quality Standards (EQS) and is inconsistent in setting similar values for foods which are very different in origin and representativeness in the total dietary exposure of consumers to cadmium, and this is not the same with raw product. It also provides values with little scientific basis which could become obstacles to the production process and would constitute a technical barrier to trade by confusing the tolerable limits, in derived or processed products for the marketing of cocoa beans (Pastor, 2017; Intriago *et al*., 2019).

In this context, the reference standard for determining cadmium levels in cocoa beans is Regulation 488/2014 (EU, 2014), which has been in force since January 2019 and establishes tolerable limits between 0,1 to 0.8 μg g^{-1} to chocolate products and has not maximum limit for unprocessed almonds or grains. This gap in the regulations leads to an inadequate methodology when applying tolerable limits of derived or processed products to the concentrations in unprocessed cocoa beans (Pastor, 2017). For this reason, other authors (Meter *et al.*, 2019) have also suggested that a maximum limit of Cd in dry grains or unprocessed cocoa mass hold be awarded, using some criteria and based on what is already set out in the current EU regulation. With the implications such as the regulatory vacuum for the producer that harm the economy and discourage the producer with the consequent possible replacement of illicit crops in the region (Alvarado, *et al*., 2020).

In this context, the objective of this work is to review and approach research on Cd levels in cocoa for major producers in Latin America; it is to contribute to the analysis of implementation, not appropriate, of the current EU regulation; on export cacaos, present an alternative calculation model and proposals for maximum limits in unprocessed almonds.

Material and Methods

In order to demonstrate and quantify the concentrations of cadmium in cocoa and cocoa derivatives, samples of cocoa were collected from three small-scale cocoa farms that also produce the first by-products of the grain, as are cocoa masses and chocolates with a high percentage of cocoa, bitter chocolate (60 and 70 %). All materials met the following protocol were processed for Cd analyses, from three (3) small cocoa-producing in the central-eastern (Miranda State), region of Venezuela.

For the categorization of total cadmium levels in unprocessed grains and compare using Regulation 488/2014 furthermore is questionable (Pastor, 2017; Meter *et al*., 2019), in the present study, fruits and products from the same batch of seeds were compared to analyze the concentration of Cd. It was analyzed in the husks of the seeds, in the bare seed, in the paste or liqueur, first product of the cocoa bean, and in the dark chocolate to 60 and 70 %. Each fraction of material: shell, endocarp or cotyledons, paste and chocolate, was digested cold and hot following the analytical route:

1) Dehydrated material (lyophilized) approx. 0.5 g dry weight addition of 5 ml HNO_3 (nitric acid) pre-digestion at room temperature for 12 h.

2) Subsequent addition of 3 ml H_2O_2 (hydrogen peroxide), 6 h.

3) Addition of 3 ml $HClO_4$ (perchloric acid) and heating to 70 degrees for 1 hour, then up to 150 degrees 1 hour.

4) Subsequently and in cold, it was brought to a final volume of 50 ml with deionized water for analysis.

5) Aqueous reference solutions were prepared by volumetric dilution of concentrated reference standards (Fisher Scientific Company, USA.) in deionized water.

The standard range was 1 to 10 mg/L (ppb). The detection limit was calculated from 10 measurements of the reagent blank processed in the same way as the samples and expressed as 3 times the standard deviation of the measurements. Limit of detection (Ld) is 0.41 μg/L. The limit of quantification (LdQ) was obtained from the same measurements as the detection limit and was estimated to be 10 times the standard deviation of these LdQ is 1.1 μg/L.

The glass material was cleaned with HNO_3 (1:1), for 24 hours and rinsed with deionized water in a equipment Atomic Absorption Spectrometer with Electrothermal source (graphite furnace), model Analytik Jena ZEEnit 700P (Germany).

This work followed the methodology according to APHA (1992), which is a manual for testing and analysis of water quality, used globally in laboratories and agencies.

For the use and modification of calculations in determining the values required by the EU, the following modifications were made, and so the formula for calculation is:

$$LCP = \frac{LCMC+LCTC}{2} \quad (1)$$

$$LCCB = \frac{FM}{RP}.VG \quad (2)$$

$$LCTC = \frac{MCP}{\%TA}.VG \quad (3)$$

Where:

LCP = Proposed Cd Limit

LCCB = Cd Limit in Cocoa Butter

LCTC = Cd Limit in Cocoa dry mass) (chocolate powder).

FM = Formula Meter's *et al*., (2019), yields a maximum limit of 1.14 μg g^{-1}

RP = Cd Reduction reported by Pastor and Gutiérrez (2016).

VG = Variability by genotype, 30 % was eliminated (applying a factor of 0.7 to the content of Cd in butter and cocoa dry mass).

MCP = Maximum for cocoa powder according to EU (0.6 μg g^{-1}).

% TA = % of unprocessed almond dry mass cake 50 % (factor 0,5).

As an example, dark chocolate with 70 % cocoa mass (0.8 μg g^{-1}), used and calculated in the formula Meter *et al.* (2019):

$$LCCB = \frac{1.14}{0.5} * 0.7 = 1.6 \text{ μg g}^{-1} \quad (4)$$

$$LCTC = \frac{0.6}{0.5} * 0.7 = 0.84 \text{ μg g}^{-1} \quad (5)$$

$$LCP = \frac{1.6 + 0.84}{2} = 1.22 \text{ μg g}^{-1} \quad (6)$$

The results obtained in the samples analyzed in this study are shown below.

Results and Discussion

A large proportion of the cocoa produced in Latin America is from small farmers whose livelihoods are particularly vulnerable to new regulations. Many are involved in the production of fine aroma cocoa, which is commonly used for products with high cocoa content and single origin products. This production is mainly destined for Europe, the first market. Therefore, short- medium- and long-term solutions are needed to mitigate the problem of high cadmium concentrations in cocoa almonds.

Cadmium is absorbed from the soil by plant roots, and air pollution. The presence of Cd in soil is a result of a combination of natural and anthropogenic processes. Natural processes include rock weathering, volcanic activity, forest fires, erosion and river sediment deposition, while anthropogenic processes include mining and industrial activities, as well as irrigation and fertilization practices, proximity to roads and roads with pollution from vehicle wear and fuels. All these factors are likely to contribute to the increase in cadmium content. Although higher concentrations of cadmium in soil may lead to a greater potential for cadmium uptake by the roots of cocoa plants, it should be noted that not all Cd in soil may be available to the plant (Ramírez, 2022). High concentrations of cadmium found in cocoa beans come from plants growing on soils with a relatively low total cadmium content. The bioavailability of cadmium to plants is influenced by a variety of soil properties: pH, organic matter content, soil texture and mineralogy, cation exchange capacity, electrical conductivity, macro and micro nutrient content and presence of micro-organisms. Alteration of some of these properties may reduce or induce the bioavailability of cadmium in cocoa plants (Ramírez, 2022). Several factors can affect the process of cadmium absorption and distribution in cocoa plants, such as tree age or plant nutrition. Particularly interesting is the variability in cadmium absorption across different cocoa genotypes, which opens up the possibility of identifying low accumulation varieties of cocoa (*Elmatsani et al*., 2024; Pastor and Gutiérrez, 2016; Pastor, 2017).

Finding alternatives to mitigate high concentrations of Cd in crops, selecting varieties with lower bioaccumulation, appropriate soils and appropriate management practices can result in the reduction of cadmium concentration in cocoa beans and therefore, in chocolate, considering actions from the crop itself to the final marketable product, reaching the specific conditions of the cocoa value chain, which favors both the producer and the consumer. Some conditions include: 1) avoid nearby areas of high risk of accumulation of heavy metals for establishment of plantations, 2) seek varieties whose natural concentration is lower (*Elmatsani et al*., 2024), 3) proper management of agricultural practices, particularly with irrigation waters, fertilization and fumigation with phosphorous products, 4) reducing cadmium levels through post-harvest processing.

Relative mobility of trace elements in soils is of paramount importance in terms of their availability and potential to leach from soil profiles into groundwater and differs depending on natural or anthropic origin (Burt *et al*., 2003; He *et al*., 2015). Due to the potential direct toxicity on biota and indirect threat to human health from ground water contamination and accumulation in crops, there is a widespread interest in the fate of heavy metals in contaminated soils, with heavy metal-combination amendments being used to immobilize or dissolve them. Heavy metals can follow different pathways: 1) they are retained in the soil, either dissolved in the water phase of the soil, occupying exchange sites or 2) they are adsorbed on inorganic constituents of the soil, associated with soil organic matter or 3) precipitated as pure or mixed solids. It is known from the physic-chemical base that metals precipitate as a result of changes in pH, oxidation and other changes in their chemical composition (Martínez and Motto, 2000). They can be absorbed by plants and thus enter the food chain, pass in to the atmosphere through volatilization and/or move between surface water and groundwater.

An important factor governing the mobility, toxicity and bioavailability of heavy metals is their speciation *i.e.* state, phases or chemical forms in which a given element is found in soil. The European Union's Community Bureau of Reference (BCR) defines soil and sediment chemical speciation analysis as the process of identifying and quantifying the different species, defined forms or phases in which an element exists in the material (Ure *et al.,* 1993; Vanderschueren *et al*., 2021).

The current EU regulation by the European Food Safety Authority (EFSA) was developed by the Scientific Panel on Contaminants in the Food Chain (CONTAM). EFSA considered it necessary to further amend the maximum levels for certain contaminants such as Cd, as set out in Regulation 1881/2006, incorporating new information and developments from the *Codex Alimentarius* (EU, 2014; Zug *et al*., 2019). The current EU regulation is based on three main aspects:

1. Dietary exposure; CONTAM conducted weekly tolerable in take studies and determined the average dietary exposure of Cd in European countries at 2.5 µg/kg bodyweight (EU, 2014; Abt and Robin, 2020). 2. Per capita consumption; high consumption of cocoa products can raise levels of cadmium in the body; and in the case of the European community, per capita consumption is three times higher than in Latin American countries. 3. ALARA principle, "As Low as Reasonably Achievable" which means as low as reasonably achievable or possible (EU, 2014).

For EFSA it is reasonable that the reduction of exposure to vulnerable consumers could be achieved by setting a maximum content for cocoa derivatives. Thus, on 12 May 2014, the Regulation 488/2014 amending Regulation 1881/2006 was approved (Table 1), adding cocoa derivatives to the list of controlled products (EU, 2014; Gramlich *et al*., 2018, Argüello *et al*., 2019; Barraza *et al*., 2019, Zug *et al*., 2019; Abt and Robin, 2020).

Table 1. Regulation 488 / 2014 controlled products derived from cocoa, was implemented in January 2019 and is currently maintained.

Cocoa Product	**Dry matter** (%)	**Maximun allowed limit** (µg * g^{-1})
Milk chocolate with a total cocoa dry matter content	< 50	0.10
Milk chocolate with a total cocoa dry matter content	≥ 30	0.30
Milk chocolate with a total cocoa dry matter content	≥ 50	0.80
Cocoa powder marketed to the final consumer or as an ingredient of sweetened cocoa powder or chocolate powder marketed to the final consumer (drinking chocolate)	*n.d.*	0.60

As mentioned above this regulation assigns a high value to chocolates with total dry matter percentage 50 %, establishes tolerable limits for Cd at final consumption, but uses arguments from the Environmental Quality Standards (EQS) and is inconsistent in setting similar values for foods which are very different in origin and representativeness in the total dietary exposure of consumers to cadmium. It also provides values with too much and too little scientific basis which could become obstacles to the production process and would constitute a technical barrier to trade by confusing the tolerable limits, in derived or processed products for the marketing of cocoa beans (Pastor, 2017; Intriago *et al*., 2019).

As the afore mentioned EU standard (Table 1) is not applicable to unprocessed whole grains, although as already explained most authors note that their found values exceed the EU set which sets a maximum of 0.8 µg g^{-1}, so it is tacitly understood that this limit is being used to classify the levels found. One of the proposals for Cd levels in grains has been established by Meter *et al*., (2019), these authors apply a proportionality ratio to the limits set in the EU Regulation and calculate a maximum limit value for Cd in raw dry grains, since the raw mass contains a similar amount of Cd as the original grains.

This proposal assumes the following concepts:

- Regulation 488/2014 is for processed products.
- The concentration of Cd in mass is similar to cocoa liquor (first derivative of processing).
- The mass % in cocoa is known.
- Butter contains minimum levels of Cd (criterion not applied in its formula).
- Proportionality.
  The calculation formula is:

$$MLCM = \frac{MLEUP}{X\ \%\ P}$$

Where:
MLCM = Maximum level of Cd in cocoa mass (μg g^{-1})
MLEUP = EU maximum level in final product (μg g^{-1})

X % P = Percentage of mass in finished product.

The example of dark chocolate with 70 % mass (dry cocoa solids), which according to the EU sets 0.8 μg g^{-1} of Cd in the finished product, so the maximum level of Cd will be:

$$MLCM = \frac{0.8}{0.7} = 1.14 \ \mu g\ g^{-1}$$

It can be seen that the EU maximum levels apply to finished products and not to raw materials. The equation estimates a maximum mass level of Cd at 1.14 μg g^{-1} which will ensure that the final product remains below the EU threshold.

This proposal is based on the calculations of Meter *et al.,* (2019) and Florida-Rofner (2021), the conclusions of Pastor and Gutierrez (2016) and Pastor (2017) and the general concepts of the average bromatological composition of chocolate and unprocessed grains; The proposal there for assumes the following concepts:

- Chemically cocoa consists of: 53.05 % cocoa factor butter used for chocolate and the difference is cocoa dry mass (cake) used for sweetened cocoa powder to and takes the factor of 0.5 (% TA).
- Bitter chocolates contain cocoa butter and on average do not exceed 50 % (Sánchez *et al*., 2016).
- In 70 % cocoa butter chocolate, the Cd content is reduced to less than half in the processing of chocolate compared to grain, so a factor of 0.5 (RP) is applied Pastor and Gutiérrez, (2016) and this work.
- The butter contains minimum levels of Cd (Meter *et al*., 2019), an aspect that was not considered in its formula and confirms what is pointed out by Pastor and Gutiérrez (2016).
- Almonds bioaccumulate cadmium in concentrations varying according to the cocoa genotype (Lanza *et al*., 2016), with a variation of approximately 30 %, which should be eliminated by applying a factor of 0.7 (VG) to partial results for cocoa butter and mass cake.
- Unpeeled cocoa beans, in one of the process steps, husking, causes the metal content to decrease (Kruszewski and Obiedzinski, 2018a, b, and this work (Table 2).

The primary processing products of the grains are approximately 50 % cocoa cake or mass used for sweetened drinking chocolate powder with an EU tolerable limit of 0.6 μg g^{-1} and cocoa butter in similar proportions to 50 %, used for chocolates with a maximum level of 0.8 μg g^{-1} (Sánchez *et al*., 2016).

The results obtained in the Cd analyses for this study are shown below (Table 2), on selected samples from three (3) farms, where the four (4) different fractions of cocoa were analyzed from the same batch of seeds before secondary products were processed.

Considering the results of the analyses, it can be observed that the greatest concentration of Cd occurs in the skin or shell Table 2, similar results as found by Kruszewski *et al*., 2018b).

Table 2. Analysis of cadmium in cocoa seed fractions and primary derived products.

COCOA FRACTIONS	Cd mg/kg	+/- *S.D.*	% RSD
Skin (shell) Hacienda 1	11.05	0.15	1.38
Skin (shell) Hacienda 2	7.50	0.55	7.06
Skin (shell) Hacienda 3	14.50	0.15	1.04
Seeds without shell Hacienda 1	1.53	0.05	3.32
Seeds without shell Hacienda 2	1.90	0.07	3.39
Seeds without shell Hacienda 3	7.55	0.05	0.67
Cocoa mass (paste) Hacienda 1	1.01	0.02	1.98
Cocoa mass (paste) Hacienda 2	0.92	0.03	2.77
Cocoa mass (paste) Hacienda 3	1.61	0.08	5.00
Chocolate Bitter 70 % Hacienda1	0.60	0.01	0.83
Chocolate Bitter 70 % Hacienda 2	0.57	0.01	1.59
Chocolate Bitter 60 % Hacienda 3	0.93	0.02	1.61

The proposal suggests that butter (Ecuation 2) and cocoa mass or paste (Ecuation 3) should be calculated separately, and in both cases genotype variation should be incorporated to reduce this partial result by 30 % by applying a factor of 0.7; finally, it must be averaged to obtain a maximum limit (Ecuation 1).

The proposed equation estimates a maximum level of Cd in unprocessed grains of 1.22 μg g^{-1} (Ecuation 6) ensuring that the finished processed product is below the EU limit (0.8 μg g^{-1}).

Relative mobility of trace elements in soils is of paramount importance in terms of their availability and potential to leach from soil profiles into groundwater and differs whether they are of natural or anthropic origin, The toxicity of metals depend not only on their concentration but also on their mobility and reactivity with other components of the ecosystem (Abollino *et al.,* 2002, He *et al*., 2015). It is therefore important to reduce by a factor of 20 % for Cd and Hg which have the highest rate of bioaccumulation.

This present proposal suggests that the formula postulated by Florida-Rofner (2021), average to obtain a maximum limit (Ecuation 1) the bio-geo-movibility factor for heavy metals should be subtracted from a factor of 0.20 to have a balance of all factors that act on the biogenesis of cadmium, so the formula would be:

$$LCP = \left(\frac{LCCB+LCTC}{2}\right) - Fbgm \qquad (7)$$

Where:

LCP = proposed Cd limit

LCCB = proposed Cd limit in cocoa butter

LCTC = Cd limit in cocoa dry mass (chocolate powder)

Fbgm = bio-geo mobility factor (0.20 for Cd)

Dark chocolate with 70 % cocoa dry mass (0,8 μg g^{-1}) is used as an example, used and calculated in the formula Meter *et al.* (2019) and Florida-Rofner (2021)

$$LCP = \left(\frac{1.6+0.84}{2}\right) - 0.20 = 1.02 \ \mu g \ g^{-1} \quad (8)$$

The proposed equation estimates a maximum level of Cd in unprocessed grains of 1,02 μg g^{-1} (Formula 8) ensuring that the finished processed product is below the EU limit (0.8 μg g^{-1}), being in accordance with some regulations such as indonesia which indicates that the cadmium limit in raw grain should be 1.00 μg g^{-1}. Kruszewski, Obiedziński, and Kowalska (2018b) investigated heavy metals (Nickel, Cadmium, Lead) in raw cocoa and chocolate products from different manufacturers, finding variable reductions during processing (10.5-33 % Cd). Similar differences were found in this study with Cd, where the metal tends to accumulate more in shell (Table 2). Low Cd uptake cocoa clones and site-specific research are therefore highly justified, as well as the environment and selected cocoa cultivars since they influence the bioconcentration of Cd in the beans.

Conclusions

The lack of maximum limits for unprocessed cocoa is perceived as a threat to the sustainability of cocoa production and has been causing some confusion and speculation. These are confusion in the scientific community when classifying unprocessed cocoa, applying the limits of the European standard for processed cocoa, a huge concern to the cocoa sector throughout our region of Latin America, and market distortions when negotiating, since the producer is hardly in a position to dispute them and buyers prefer low Cd contents to guarantee their use in any recipe, with the consequent negative effect on the price received for grain. It has been shown that there is discrimination in the accumulation of metals, and the concentration in bare grain is much lower. It is also possible to consider the genetics of the variety harvested and the origin of the soil that supports them. Therefore, the calculations cannot be made considering a seed (or grain) with its cover and the genotype.

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Bibliographic References

Abollino O., Aceto M., Malandrino M., Mentasti E., Sarzanini C., Barberis R. (2002). *Distribution and mobility of metals in contaminated sites*. Chemo metric Investigation of Pollutant Profiles. *Environmental Pollution*, 119 (2), 177-193. DOI: 10.1016/S0269-7491(01)00333-5

Abt E., Robin L. P. (2020). *Perspective on cadmium and lead in cocoa and chocolate.* Journal of Agricultural and Food Chemistry, 68, 13008-13015. DOI: 10.1021/acs.jafc.9b08295

Alvarado Y., Ferrer R., Florida-Rofner N. (2020). *Evaluación ex post al proyecto productivo alternativo de Bella Bajo Monzón*. Ciencia Unemi, 13(34), 47-58. ISSN electrónico 2528-7737.

Antoine, J. M. R., Fung, L. A. H., Grant, C. N. (2017). *Assessment of the potential health risks associated with the aluminium, arsenic, cadmium and lead content in selected fruits and vegetables grown in Jamaica.* Toxicology reports. 4, 181-187. DOI: 10.1016/j.toxrep.2017.03.006

APHA. 1992. *Standard Methods for the Examination of Water and Wastewater*. 18th edition. American Public Health Association (APHA), American Water Works Association (AWWA) and Water Pollution Control Federation (WPCF), Washington, DC.

Argüello, D., Chávez, E., Lauryssen, F., Vanderschueren, R., Smolders, E., Montalvo, D. (2019). *Soil properties and agronomic factors affecting cadmium concentrations in cacao beans: A nationwide survey in Ecuador*. Science of The Total Environment, 49, 120-127. doi.org10. 1016j.scitotenv.2018.08.22

Barraza, F., Moore, R. E. T., Rehkämper, M., Schreck, E., Lefeuvre, G., Kreissig, K., Coles, B. J., Maurice, L. (2019). *Cadmium isotope fractionation in the soil–cacao systems of Ecuador: a pilot field study*. Royal Society Chemistry (RSC)Advances, 9, 34011-34022. DOI: 10.103c9ra05516a

Burt R., Wilson M. A., Mays M. D., Lee C. W. (2003*). Major and trace elements of selected pedons in the USA*. Journal of Environmental Quality, 32(6), 2109-21. https://doi.org/10.2134/jeq2003.2109

Elmatsani, H. M., Munarso, J., Rahardjo, Y. P., Benyamin, B. O., Sjafrina, N., Astut, P., Arianto, A., Lukas, A., Djafar, M. J. (2024). *Reducing Cadmium and Lead Contamination in Cacao: A Bibliometric Analysis of 10 Years of Research Using Bibliometrics.* BIO Web of Conferences. 101, 01011 https://doi.org/10.1051/bioconf/202410101011 5th ICOLIB.

Engbersen, N., Gramlich, A., López, M., Schwarz, G., Hattendorf, B., Gutiérrez, O., Schulin, R. (2019*). Cadmium accumulation and allocation in different cacao cultivars*. Science of the total environment*,* 678(8), 660-670. 10.1016/j.scitotenv.2019.05.001

Florida-Rofner, N. (2021). *Review on maximum limits of cadmium in cocoa (Theobroma cacao* L.*)*. La Granja, 34 (2), 117-130. http://doi.org/10.17163/lgr.n34.2021.08

Gramlich, A., Tandy, S., Gauggel, C., López, M., Perla, D., González, V., Schulin, R. (2018). *Soil cadmium uptake by cocoa in Honduras*. Science of the Total Environment. 612, 370-378. https://doi.org/10.1016/j.scitotenv.2017.08.145

He, S., He, Z., Yang, X., Stoffella, P. J., Baligar, V. C. (2015). *Soil biogeochemistry, plant physiology, and phytoremediation of cadmium-contaminated soils*. Advances in agronomy. 34, 135-225. doi.org/10.1016/bs.agron.2015.06.005

Intriago, F. G., Talledo, M. V., Cuenca, G. J., Macías, J. R., Álvarez, J. R., Menjívar, J. C. (2019). *Evaluation of heavy metal content in cocoa almonds (Theobroma cacao* L.*) during the beneficiary process*. PRO-SCIENCES: Revista de Producción, Ciencias e Investigación, 3, 17-23. E-ISSN: 2588-1000.

Khan, A., Khan, S., Khan, M. A., Qamar, Z., Waqas, M. (2015). *The uptake and bioaccumulation of heavy metals by food plants, their effects on plants nutrients, and associated health risk: a review.* Environ Sci. Pollut. Res. 22:13772–13799. DOI 10.1007/s11356-015-4881-0

Kruszewski, B., Obiedziński, M. W. (2018a). *Multivariate analysis of essential elements in row cocoa and processed chocolate mass material from three different manufactures*. LWT- Food Science and Technology 98, 113-123. doi.org10.1016 J.lwt.2018.08.030

Kruszewski, B., Obiedziński, M. W., Kowalska, J. (2018b). *Nickel, cadmium and lead levels in raw cocoa and processed chocolate mass materials from three different manufacturers.* Journal of Food Composition and Analysis, 66, 127-135. DOI: 10.1016/j.jfca.2017.12.012

Lanza, J. G., Churión, P. C., Liendo, N. J., López, V. H. (2016). *Evaluación del contenido de metales pesados en cacao (Theobroma cacao* L.*) de Santa Bárbara del Zulia, Venezuela.* Saber, 28(1), 106-115. http://ve.scielo.org/scielo.php?script=sci_arttext&pid=S1315-01622016000100011&lng=es&nrm=iso>. ISSN 2343-6468.

Maddela, N. R., Dhatri Kakarla D.,García, L. C., Chakraborty, S., Kadiyala Venkateswarlu, K., Megharaj, M. (2020). *Cocoa-laden cadmium threatens human health and cacao economy: A critical view.* Science of The Total Environment 720, 2020, 137645. http://doi.org/10.1016/j.scitotenv.2020.137645

Martínez, C. E., Motto, H. L. (2000). *Solubility of lead, zinc and copper added to mineral soils*. Environmental Pollution. 107(1), 153-158. https://doi.org/10.1016/S0269-7491(99)00111-6

Meter, A., Atkinson, R., Laliberte, B. (2019*). Cadmio en el cacao de América Latina y el Caribe. Análisis de la investigación y soluciones potenciales para la mitigación*. 84 pp. Biodiversity International. Online: https://bit.ly/3baF nwA. ISBN:978-92-9255-136-0

Pastor, S., (2017). *Niveles de cadmio en el chocolate: NM y ECA, sí; OTC, no*. In: International Symposium on Cocoa Research (ISCR). pp, 1-5.

Pastor, S., Gutiérrez, M. (2016). *Sobre los fundamentos de una norma que regula el cadmio en los alimentos y presume del mismo en el suelo.* Memorias del XXI Congreso Latinoamericano de la Ciencia del Suelo. pp, 24-28.

Ramírez, R., (2022*). Contaminación de suelos y cultivos con metales pesados y nutrientes en Venezuela*. Revista Facultad Agronomía (UCV). 48: 01 - 17.

Reyes, Y., Vergara, I., Torres, O., Díaz, M., González, E. E. (2016). *Contaminación por metales pesados: Implicaciones en salud, ambiente y seguridad alimentaria*. Ingeniería Investigación y Desarrollo: I2+ D. ISSN-e 2422-4324, ISSN 1900-771X. 16 (2), 66-77.

Sánchez, A. S., Naranjo, J. A., Córdova, V., Ávalos, D. A., Zaldívar, J. M. (2016). *Caracterización bromatológica de los productos derivados de cacao (Theobroma cacao* L.*) en la Chontalpa, Tabasco, México*. Revista Mexicana de Ciencias Agrícolas, 7 (14), 2817-2830.

Unión Europea-UE. Regulation No. 488/2014. (2014). *They modify EC Regulation No 1881/2006 regarding the maximum content of cadmium in food products*. Official Journal of the European Union. Online: https://bit.ly/3uvfOxT

Ure A. M., Quevauviller Ph., Muntau H., Griepink B. (1993). *Speciation of Heavy Metals in Soils and Sediments. An Account of the Improvement and Harmonization of Extraction Techniques Undertaken Under the Auspices of the BCR of the Commission of the European Communities*. International Journal of Environmental Analytical Chemistry, 51, 135-151. https://doi.org/10.1080/03067319308027619

Vanderschueren R., Argüello D., Blommaert H., Montalvo D., Barraza F., Maurice L., Schreck E., Schulin R., Lewis C., Vázquez J., Umaharan P., Chávez E., Sarret G., Smolders E. (2021). *Mitigating the level of cadmium in cacao products: Reviewing the transfer of cadmium from soil to chocolate bar*. Science of the Total Environment, 781, 146779. https://doi.org/10.1016/j.scitotenv.2021.146779

Zug K. L. M., Huamani Yupanqui, H. A., Meyberg F., Cierjacks J. S., Cierjacks A. (2019). *Cadmium accumulation in Peruvian cacao (Theobroma cacao* L.*) and opportunities for mitigation*. Water, Air, and Soil Pollution, 230, 1-18. 10.1007/s11270-019-4109-x

List of abreviations

Cd = Cadmium
MLCM = Maximum level of Cd in cocoa mass (µg g^{-1}).
MLEUP = EU maximum level in final product (µg g^{-1}).
X % P = Percentage of mass in finished product.
LCP = Proposed Cd Limit.
LCCB = Cd Limit in Cocoa Butter.
LCTC = Cd Limit in Cocoa dry mass) (chocolate powder).
FM = Meter's Formula *et al*., (2019), yields a maximum limit of 1.14 µg g^{-1}
RP = Cd Reduction reported by Pastor and Gutierrez (2016).
VG = Variability by genotype, 30 % was eliminated (applying a factor of 0,7 to the content of Cd in butter and cocoa dry mass).
MCP = Maximum for cocoa powder according to EU (0.6 µg g^{-1}).
% TA = % of unprocessed almond dry mass cake 50 % (factor 0.5).

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