

Cadmium in cacao: variability among laboratories and ready-for-sale beans

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ABSTRACT

- Variability among different laboratories in Ecuador and Colombia was quantified based on the results of a proficiency test with six cacao samples and four soil samples.
- Ready-for-sale beans were sampled from different cacao warehouses to determine the variability among beans at different levels. The results form a base for a future sampling protocol to determine cadmium (Cd) in ready-for-sale beans.

1. Variability among laboratories in Ecuador and Colombia

INTRODUCTION

Two proficiency tests were organized to

- Quantify the variability among Ecuadorian and Colombian laboratories.
- Set up an accreditation scheme for laboratories that performed well.
- Help laboratories by organizing training sessions and writing guidelines.

Muestra interna de referencia KUL 1	Muestra interna de referencia KUL 2	Muestra interna de referencia KUL 3	Muestra interna de referencia KUL 7	Muestra interna de referencia KUL 8
Muestra interna de referencia KUL 4	Muestra interna de referencia KUL 5	Muestra interna de referencia KUL 6	Muestra interna de referencia KUL 9	Muestra interna de referencia KUL 10

METHODS

Two proficiency tests $\left\{ \begin{array}{l} 6 \text{ cacao samples} \\ 4 \text{ soil samples} \end{array} \right\}$ 34 laboratories in total

Acceptable results according to ISO standards: z'-scores between -2 and 2

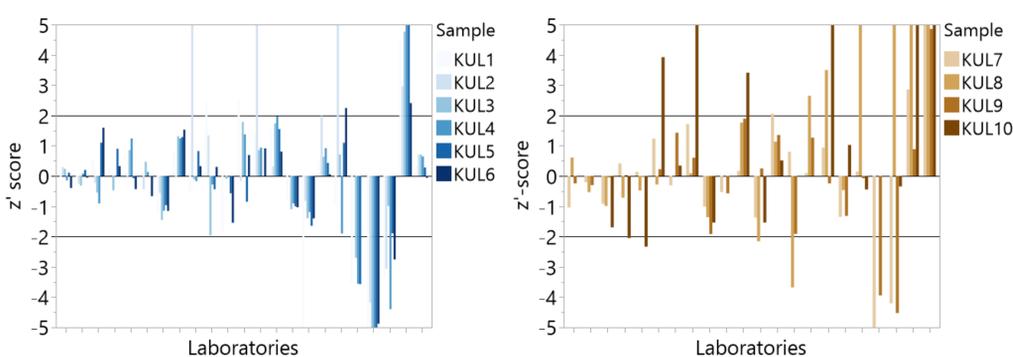
$$z'_i = \frac{x_i - x_{nt}}{\sqrt{\sigma_{nt}^2 + u^2(x_{nt})}}$$

With
 x_{nt} = median
 σ_{nt} = MADe
 $u(x_{nt})$ = uncertainty on x_{nt}

Variability between laboratories: robust coefficient of variation $rCV = \frac{x_{nt}}{\sigma_{nt}}$
 Robust statistics to decrease the effect of extreme outliers

RESULTS

Z'-scores for cacao samples (left) and soil samples (right)



11/23 all acceptable
 7/23 one sample unacceptable
 5/23 two or more unacceptable

7/22 all acceptable
 10/22 one sample unacceptable
 5/22 two or more unacceptable



Variability between laboratories: $rCV = 24\%$ (and $CV = 46\%$)

CONCLUSION

- 24 % of the laboratories reported acceptable results for all samples, 44 % reported one unacceptable result, 24 % reported more than one unacceptable result.
- Variability between laboratories is high ($rCV = 24\%$ and $CV = 46\%$)
- Questionnaire: most of the underperforming laboratories did not use certified reference materials, ultrapure water and did not correctly calculate LOD/LOQ
 → Informative sessions + QA/QC guidelines

2. Variability among ready-for-sale beans

INTRODUCTION

An official sampling protocol for Cd in ready-for-sale beans packed in jute bags on wooden pallets does not exist. Therefore, a lot of different methods are used in practice. These methods are often not specifically designed for Cd, but they are for general sampling of cacao beans. In this study, the variability in Cd concentration among beans was quantified to serve as a starting point for a future sampling protocol.

METHODS

Four cacao batches were sampled to determine the variability in Cd concentration (1) among beans in one bag, (2) among bags on one pallet, and (3) for two sampling strategies.

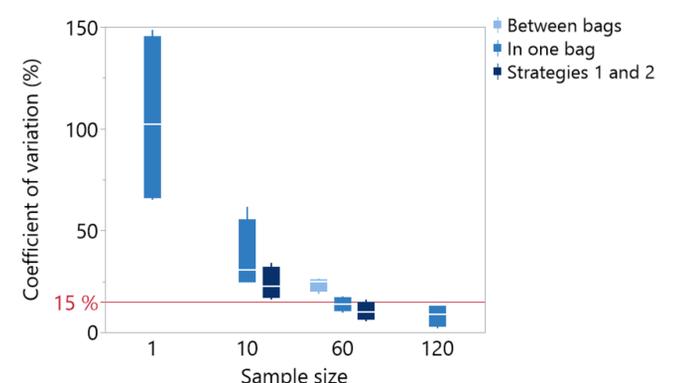


One "batch" = several pallets with 30 jute bags of approximately 70 kg of dried cacao beans

Strategy 1: sample 30 beans from 20 bags of one pallet and mix manually, then homogenize 10 beans in a blender and take a subsample from this powder.
 Strategy 2: similar but homogenize 60 beans.

RESULTS

- Variability decreases with the square root of sample size: very important
 → Homogenize at least 60 beans
- Variability in a bag is 10% lower than variability among bags (systematic filling)
 → Sample at least 10 bags



CONCLUSION

At least 60 beans should be homogenized from a subsample that was taken from at least 10 bags to obtain a reliable Cd concentration for the cacao on one pallet (~2 tons). These results form a good basis for a future sampling protocol for ready-for-sale cacao. They are also a guideline for laboratories receiving or analyzing samples for Cd analysis.

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