Cadmium in cacao: variability among laboratories and ready-for-sale beans  
I. Dekeyrel and E. Smolders  
Department of Earth and Environmental Sciences, Division of Soil and Water Management, KU Leuven

ABSTRACT

1. 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.
2. 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.

INTRODUCTION

Two proficiency tests were organized to
(1) Quantify the variability among Ecuadorian and Colombian laboratories.
(2) Set up an accreditation scheme for laboratories that performed well.
(3) Help laboratories by organizing training sessions and writing guidelines.

METHODS

Two proficiency tests  
6 cacao samples  
4 soil samples  
34 laboratories in total

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

\[ z'_i = \frac{x_i - x_{\text{ref}}}{\sqrt{\sigma_{i\text{ref}}^2 + u^2(x_{\text{ref}})}} \]

With  
\( x_{\text{ref}} \) = median  
\( \sigma_{i\text{ref}} \) = MADe  
\( u(x_{\text{ref}}) \) = uncertainty on \( x_{\text{ref}} \)

Variability between laboratories: robust coefficient of variation \( rCV = \frac{\text{mean}}{\sigma_{\text{ref}}} \)

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

10/22 all acceptable  
7/22 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

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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