# Enhancing plant geochemistry characterization by combining trace element measurements and analytical uncertainties

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## Introduction

- A typical challenge for plant analysis are trace element concentrations close to the nominal zero.
- Values should always be reported along with the associated uncertainty. It is not recommended to report values below limit of detection $L_D$, as '<$L_D$' or as zeros (e.g. Currie 1999; Ulianov et al. 2016).
- We propose to account for uncertainties by Bayesian statistics, considering several components.
- A hierarchical Bayesian model is used to incorporate the uncertainties of each measurement and produce a best estimation of mean of concentrations (close to zero).

## Method and Data

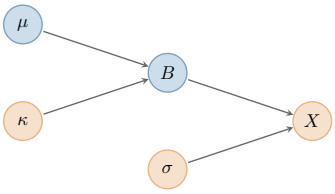
### Statistics

The Rocke-Lorenzato model is a descriptive two-component model of measurment uncertainties:

$$x \sim N(\mu, \sigma^2 + \kappa^2\mu^2)$$

The corresponding Bayesian model is:

$$X = A + B \cdot \mu$$




$$A \sim N(0, \sigma^2)$$

$$[B|\mu,\kappa] \sim LN(\nu, \sigma_B^2)$$

$$[X|B,\sigma] \sim N(B, \sigma^2)$$

The expected value and the CV of *B* are

$$E[B] = 1 = \exp(\nu + \frac{1}{2}\sigma_B^2) \qquad \frac{Var[B]}{\mu^2} = \kappa^2 = \exp(\sigma_B^2) - 1$$

The Bayesian updating formula is

$$P_\mu(\mu|x) \propto L(x|\mu) \cdot P_\mu^0(\mu)$$

and the likelihood associated to the model is

$$L(x|\mu) = \int_{\mathbf{R}^+} f_x(x|b,\sigma) \cdot f_B(b|\kappa)\, db$$

### Analytical Method and Data

16 rye samples were collected as whole plants (aboveground plant parts without roots) at two locations in 2015 and 2016. The samples had been dried at at 105C and were cut in a universal cutting mill to < 0.5 mm. Aliquots of 700 mg of plant powder were completely digested with a mixture of ultra-pure concentrated $HNO_3$, $HClO_4$, and HF in closed ultra-clean PTFE vessels and then fill up to 50 mL for the analytical solution. In the resulting clear sample solutions 47 elements were quantified by ICP-OES (Agilent 5100 VDV) and ICP-MS (Thermo Scientific iCAP Q).

## Results

Four methods of calculating a mean are compared:

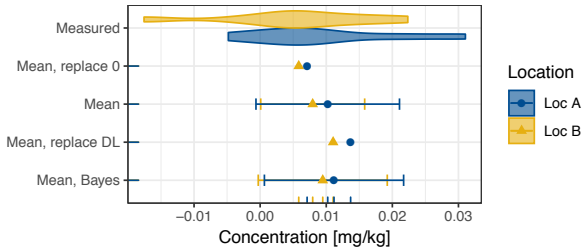
I) the 'classical' mean

II) mean with values below $L = 3 \cdot \sigma_{Blinds}$ replaced by $L$

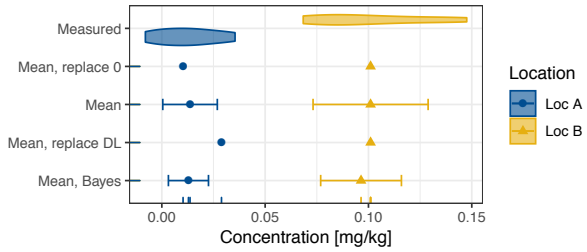
III) mean with values below $L$ replaced by 0

IV) mean based on Bayesian method proposed here

### Cobalt (Co)




### Tungsten (W)




## Conclusion

The approach allows to use all measured data, regardless of limits of detection. Based on Baysian statistics it exploits the knowledge about

- sources of uncertainties,
- knowledge about priori probability and
- QC data like replicate measurements/ SRM/ CRM

to calculate an estimate of mean of measurements.

## Citations

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