Combining trace element measurements with analytical uncertainties for a better characterization of plant geochemistry

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Trace element analysis in plants is often subject to a high measurement uncertainty and accordingly the variability of the geochemical composition of trace elements in plants is – especially close to the detection limit - very high. In this contribution we propose a method to estimate models respecting the uncertainty and capable of treating values below and around the detection limit. We suggest to use all measurement signals, but report it alongside with the individual uncertainties for each value. The standard descriptive and statistical analysis mainly ignores these uncertainties by simply reporting if a signal value is below the detection limit (BDL) or above. BDL-values are either ignored or replaced by an arbitrary small value. In both cases this can substantially distort the analysis. Our methodology could substantially reduce this bias.

In order to take into account the constraints of concentration data we use methods of compositional data analysis, i.e. represent population by their compositional expectation, typically represented in an log-ratio transform. The uncertainties are incorporated in statistical methods by estimating the reported value not by a simple mean, but by an estimation procedure using the model assumption that a signal observed in the geochemical analysis has two components of variability: i) A population spread that could e.g. be modeled by a compositional distribution, and ii) a signal variability to be modeled according to the measurement instrument, typically assuming additive normal or Poisson errors and calibration errors. The parameters for the model of the signal variability are estimated from blind values, duplicate analysis as well as precision and accuracy of repeatedly measured reference samples.

We will present the change of results produced by the methodology over a standard approach with reporting BDL-values by demonstrating the applicability of the methodology with simulated data and a dataset of rye, ryegrass, faba bean, triticale and amaranth from two agricultural test sites in Germany. All samples had been treated by a four-acid digestion and analyzed by ICP-MS and ICP-OES.