EVALUATION OF SAMPLING UNCERTAINTY IN THE DETERMINATION OF TOTAL ORGANIC CARBON, AVAILABLE SULFUR, AND NITRATE NITROGEN IN SOILS

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RELEVANCE

Organic carbon (TOC), sulfur (S), and nitrate nitrogen (N-NO_3) are key indicators of soil fertility and fundamental components of biogeochemical cycles. Accurate and reliable quantification of these parameters is an essential prerequisite for agrochemical monitoring, reasoned calculation of fertilizer application rates, and environmental assessment, placing high demands on the reliability of results at all stages of the analytical process.

Primary sampling and physical sample preparation are well known to introduce additional sources of measurement uncertainty and neglecting such a critical component can lead to wrong conclusions.

The aim of the study was to evaluate soil sampling uncertainty in the determination of organic carbon, the mass fraction of available sulfur, and the mass fraction of nitrate nitrogen.

RESULTS

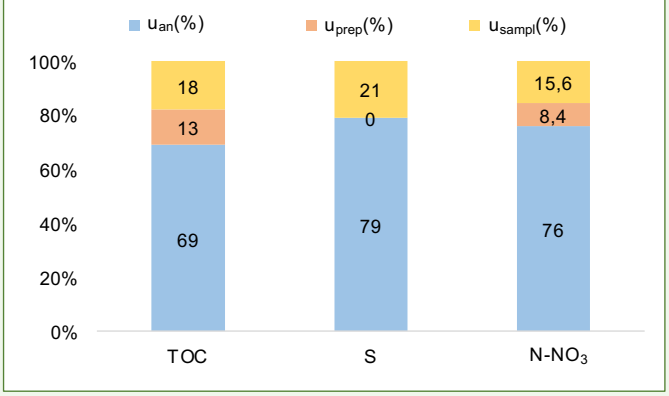
Data processing was performed by analysis of variance (ANOVA) following a three-factor hierarchical design in accordance with ISO 5725-3.

Components of the measurement uncertainty budget.

Uncertainty source	Analyte		
	TOC	S	N-NO_3
Primary sampling, u_{sampl}(%)	5,8	32	16
Physical sample preparation, u_{prep}(%)	1,1	0	1,8
Analytical uncertainty, u_{an}(%)	1,5	8,4	3,3
Combined standard uncertainty, u_c(%)	6,1	34	16
Expanded uncertainty, U(%) (k = 2)	12	67	33

* $u_c = \sqrt{u_s^2 + u_{prep}^2 + u_{an}^2}$

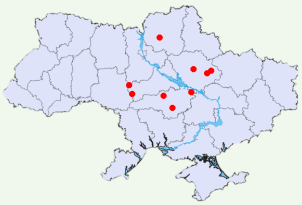
Relative contribution of uncertainty components to the combined uncertainty.



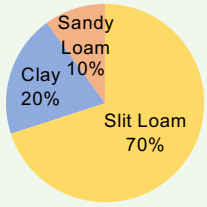
MATERIALS AND METHODS

The experiment was carried out in accordance with the recommendations of the Eurachem guide [2].

Ten sites from different regions of Ukraine (k = 10) were selected for the study. The samples included soils of various textures: loams, clays, and sandy loams. At each location, duplicate soil samples were collected in parallel (l = 2) according to ISO 10381-4:2003.

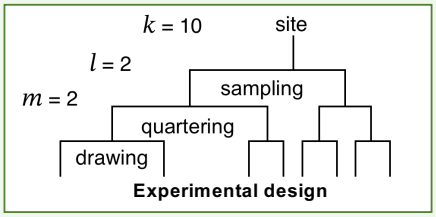


Sampling locations



Texture of soil samples

Sample preparation was performed in accordance with ISO 11464:2006. The total volume of the sample was divided in half during the quartering stage (m = 2) and the drawing of analytical test portions (n = 2) to obtain duplicate results. Thus, the experimental scheme was a fully nested $k \times l \times m \times n$ design.



Experimental design

The determination of the selected analytes in soil was carried out using the following methods:

- total organic carbon by dry combustion according to ISO 10694:2001);
- available sulfur by optical emission spectrometry following calcium chloride extraction (according to an in-house validated method);
- nitrate nitrogen spectrophotometrically by absorbance in the ultraviolet spectral range following calcium chloride extraction (according to an in-house validated method)

CONCLUSIONS

It was established that for all investigated analytes, sampling uncertainty (u_{sampl}) is the dominant component of measurement uncertainty in terms of both absolute and relative contributions. Conversely, the contribution of the physical sample preparation stage (u_{prep}) is minimal and makes no noticeable contribution to the overall metric.

Considering the obtained results, neglecting the contribution of sampling leads to a substantial underestimation of the overall measurement uncertainty.

REFERENCES

[1] M. H. Ramsey, S. L. R. Ellison, P. Rostron (eds.) Eurachem/EUROLAB/CITAC/Nordtest/AMC Guide: Measurement uncertainty arising from sampling: a guide to methods and approaches, Second ed. Eurachem, 2019. Available from http://www.eurachem.org

[2] M. H. Ramsey, P. D. Rostron, F. C. Raposo (eds.) Eurachem/EUROLAB/CITAC/ Nordtest/AMC Guide: Validation of Measurement Procedures that Include Sampling. Eurachem, 2024. Available from http://www.eurachem.org