Evaluation of measurement uncertainty of environmental matrices indicators including sampling uncertainty

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INTRODUCTION

- ✓ Testing laboratories are interested in estimating measurement uncertainties (MU) of indicators of environmental matrices. The main reasons for that are requirements of accreditation bodies, legal regulations and customers. Uncertainties reported by the laboratory quite often do not include sampling uncertainties and do not respect the effect of the concentration level of analytes. A laboratory validation study suitable to evaluate MU, which would include sampling and analysis, would entail significant financial and time costs and include only in-house experiment.
- ✓ Obtaining the estimation of real values of uncertainties achieved in the analysis of environmental samples is a challenging task and the targeted interlaboratory experiment is an effective way to obtain such estimates of measurement uncertainty values, including sampling.

EXPERIMENTAL PART

- ✓ Several interlaboratory experiments focusing on different matrices were organized in previous years: sludge (2016), waste (2017), sediments (2018), and surface and raw water (2019). Analytes of interest and results from 2018 and 2019 are shown in tables in the results section.

Assessment of samplers

A control sample prep

Sediment sampling

Water sampling

On-site measurement

- ✓ Statistical model for measurement uncertainty evaluation based on an empirical approach for estimating the MU and statistical procedures in the Eurachem/CITAC Guide [1] was chosen. In nutshell the standard uncertainty *u* was estimated using standard deviation s_{meas}, which is given by:

$$u = s_{meas} = \sqrt{s^2_{sampling} + s^2_{analytical}}$$

RESULTS

Results obtained for two particular matrices are presented in tables 1-2. Short discussion of interesting outcomes is presented in conclusions.

Table I. Results of selected indicators – raw and surface water from 2019

Parameter	Unit	Robust* mean from PT	Determined value**	Determined value***	U´samp [% rel.]	U´anal [% rel.]	U´meas [% rel.]	U´samp [% rel.]	U´anal [% rel.]	U´meas [% rel.]
						ANOVA			RANOVA	
pH	-	7.65	7.64	7.64	4.38	0.66	4.43	2.91	0.54	2.96
Conductivity	mS/m	36.7	36.5	36.5	6.59	1.28	6.71	4.41	0.85	4.49
Total P	mg/L	0.29	0.29	0.29	23.41	6.51	24.30	16.45	7.10	17.92
Total N	mg/L	2.6	2.6	2.6	21.28	11.14	24.02	14.46	7.12	25.47
Clorides	mg/L	29.8	29.9	29.9	15.02	4.12	15.57	17.28	2.00	17.39
Sulphates	mg/L	35.7	36.0	35.6	17.96	8.15	19.73	15.56	3.86	16.03
Ca	mg/L	35.6	35.9	35.4	18.53	5.99	19.48	13.57	6.56	15.07
Mg	mg/L	10.2	10.2	10.2	13.09	7.81	15.24	8.20	6.52	10.47
Fe	mg/L	0.47	0.48	0.48	31.28	8.06	32.31	24.03	7.51	25.18
Mn	mg/L	0.25	0.25	0.25	22.03	13.61	25.89	24.49	11.50	27.06
TOC	mg/L	10.3	10.2	10.3	25.92	4.11	26.24	24.89	4.61	25.32

Table II. Results of selected indicators in mg/kg of dry matter– sediments 2018

Parameter	Limit value in local legislation	Robust* mean from PT	Determined value**	Determined value***	U´samp [% rel.]	U´anal [% rel.]	U´meas [% rel.]	U´samp [% rel.]	U´anal [% rel.]	U´meas [% rel.]
						ANOVA			RANOVA	
As	30	25.9	25.8	26.06	18.31	11.39	21.56	16.70	7.93	18.48
Ba	600	129	124	125	17.36	8.18	19.19	15.42	8.10	17.42
Be	5	1.09	1.00	0.99	27.91	12.93	30.47	28.35	3.87	28.62
Cd	2.5	0.476	0.485	0.465	27.43	20.33	34.14	18.56	18.40	26.13
Co	30	8.37	7.78	7.87	24.32	7.51	25.45	22.50	7.78	23.81
Cr	200	37.5	35.5	35.8	25.91	8.66	27.46	25.06	8.55	26.47
Cu	100	24.34	22.94	22.94	23.06	8.11	24.45	23.29	6.99	24.32
Hg	0.80	0.077	0.079	0.078	14.79	9.79	17.74	13.68	8.97	16.35
Ni	80	22.2	22.2	21.2	18.45	14.54	23.49	20.50	9.76	22.70
Pb	100	42.7	40.9	40.9	29.31	14.5	32.71	26.64	9.78	28.38
V	180	45.6	43.2	43.01	22.13	6.94	23.20	20.67	5.81	21.47
Zn	600	99	93	93	24.36	8.73	25.88	22.94	7.59	24.16
Dry matter	-	42.7	42.6	42.6	27.20	3.57	27.43	22.46	3.18	22.69

***** ISO 13528. Hampel estimator; ****** Value evaluated from ANOVA; *** Value evaluated from RANOVA.

CONCLUSIONS

A brief summary of findings for individual matrices and interlaboratory comparisons organized by an accredited proficiency testing provider (CSlab, Ltd.) in 2016-2019 has revealed:

- ✓ A comparison of the results processed by ANOVA and RANOVA confirmed that robust methods should be used when clear outliers appear.
- ✓ Laboratories with a better technical equipment and well-established internal quality control system report lower MUs, which puts them at a disadvantage compared to laboratories with a higher MU, often estimated by a "qualified estimate".
- ✓ Laboratories usually do not have evaluated uncertainties for different concentration levels of analytes, the uncertainty has been reported as a constant value (i.e. not concentration dependent).

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References

[1] Michael H. Ramsey, Stephen L. R. Ellison (eds). Measurement uncertainty arising from sampling. A guide to methods and approaches. 1st Ed. 2007. ISBN 978-0-948926-26-6.