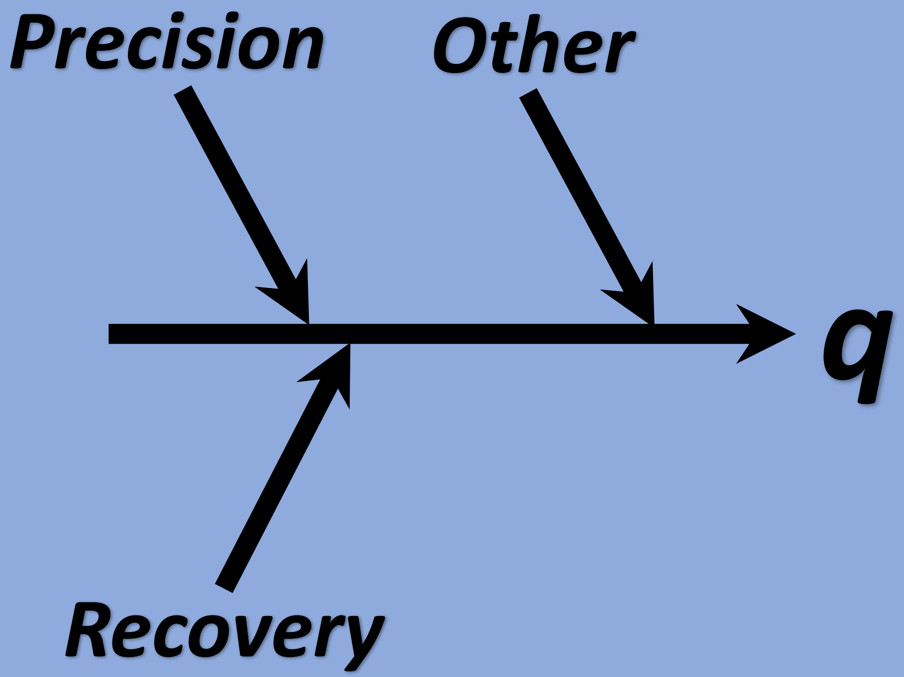
The impact of input data on the evaluation of the measurement uncertainty:

A case study



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Outline

(1) Method validation and MU* evaluation

(2) Principles of MU evaluation from in-house validation

(3) MU models for the determination of total As in sediments

(4) Final remarks

*** - measurement uncertainty**

Method validation

Method validation involves proving that the method is applicable to an adequate scope (e.g. matrices diversity and analyte level interval) and frequently produced measurements with an adequately low MU.

Additional requirements can be defined:

- **Analysis cost**
- **Analysis duration**
- **Required resources**
- **Other**

Measurement uncertainty

VIM 3 definition of MU:

BLAH BLAH BLAH , based on the information used.

The MU expresses more than the measurement performance and the quality of used references…it expressed how available performance data was considered to evaluate measurements quality

1. JCGM, International Vocabulary of Metrology, BIPM, 2012.

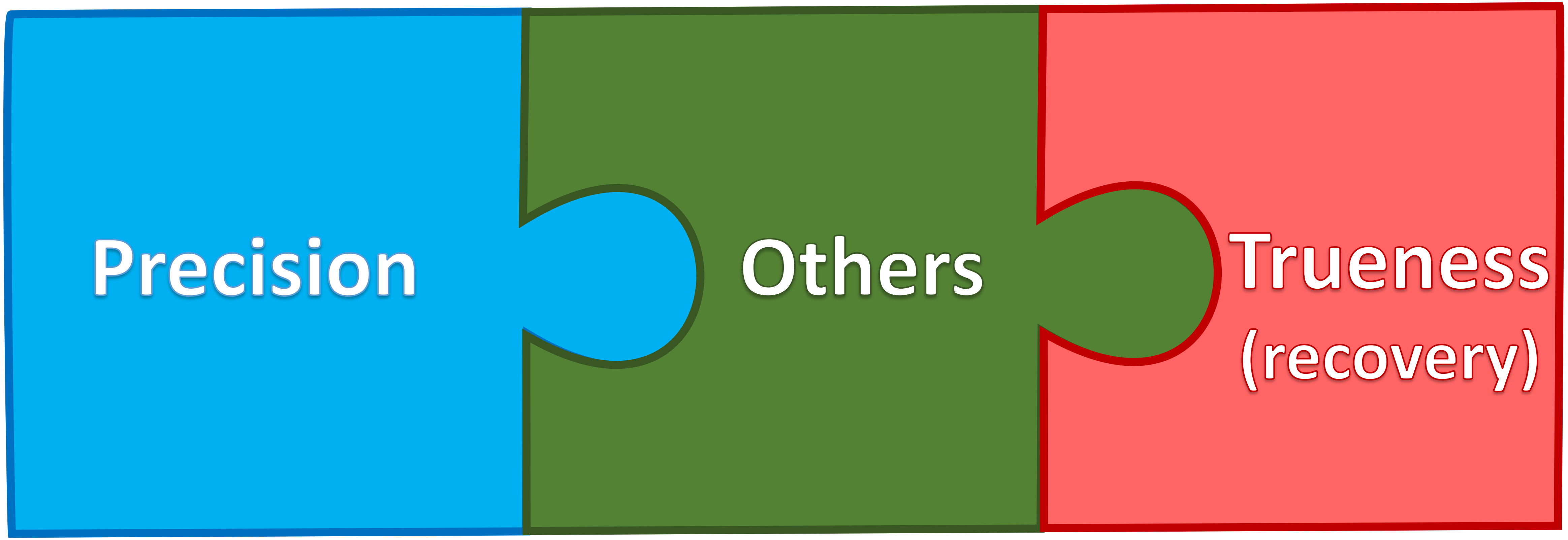
Measurement uncertainty

Never underevaluate the MU

Try not to overevaluate MU too much

MU from in-house validation data

Uncertainty components



MU from in-house validation data

- **At low analyte levels (< 2c_{LOQ} to 5c_{LOQ}):**

$$U^{95} = 2\sqrt{u_{\mathrm{P}}^2 + u_{\bar{R}}^2 + u_{0}^2}$$

- **At higher analyte levels (> 2c_{LOQ} to 5c_{LOQ}):**

$$U^{95} = 2c_{\mathrm{S}}\sqrt{u_{\mathrm{P}}'^2 + u_{\bar{R}}'^2 + u_{0}'^2}$$

where u and u' are absolute and relative standard uncertainties, U^{95} is an expanded uncertainty for 95% confidence level and c_{S} is the sample concentration.

MU from in-house validation data

Precision uncertainty, u_{P}:

$$u_{\mathrm{P}} = \sqrt{\frac{s_{\mathrm{I}}^2}{p} + \frac{s_{\mathrm{r}}^2(1-n)}{pn}}$$

where u_{P} is the precision standard uncertainty from the mean of pn values estimated from analysis performed in p days where in each day n replicates were obtained.

s_{I} and s_{r} - Intermediate and repeatability standard deviations.

(for $p = 1$ and $n = 1$, $u_{\mathrm{P}} = s_{\mathrm{I}}$)

MU from in-house validation data

Trueness uncertainty, $u_{\bar{R}}$: **PART I**

Evaluated from the analysis of *N* reference materials:

$$\bar{\bar{R}} = \frac{\sum_{i=1}^{N} \bar{R}_i}{N}$$

$$u_{\bar{\bar{R}}} = \frac{\sqrt{\sum_{i=1}^{N} u_{\bar{R}(i)}^2}}{N}$$

CRM and spiked samples without native analyte:

$$u_{\bar{R}(i)}^2 = \bar{R}_i^2 \left[\left(\frac{s_{\mathrm{I}}(c_i)}{\bar{c}_i \sqrt{n_i}} \right)^2 + \left(\frac{u(C_i)}{C_i} \right)^2 \right]$$

Spiked samples with native analyte:

$$u_{\bar{R}(i)}^2 = \bar{R}_i^2 \left[\frac{s_{\mathrm{r}}^2(c_i)/n_i + s_{\mathrm{r}}^2(c_{oi})/m_i}{(\bar{c}_i - c_{io})^2} + \left(\frac{u(C_{+i})}{C_{+i}} \right)^2 \right]$$

MU from in-house validation data

Trueness uncertainty, $u_{\bar{R}}$: **PART II**

Assessment of the deviation between $\bar{\bar{R}}$ and 1:

$$\frac{\left|1-\bar{\bar{R}}\right|}{u_{\bar{\bar{R}}}} < 2$$

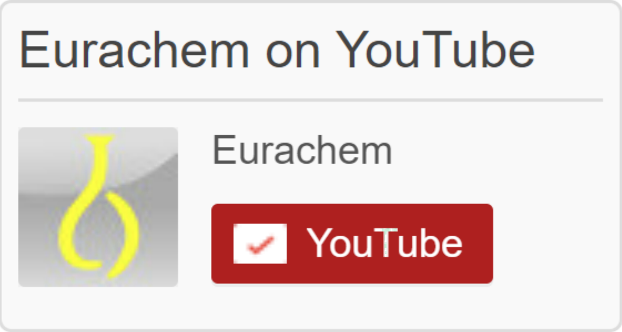
Yes → **No need to correct for recovery**

No → **Correct for recovery if allowed**

MU from in-house validation data

Trueness uncertainty, u_T: PART II

Assessment of the deviation between $\bar{x}$ and 1:



No → Correct for recovery if allowed

MU from in-house validation data

Case study: **Problem description**

The Portuguese law establishes maximum As contamination for some sediment uses and dredging practices

Total As, *w* (mg kg^{-1})

Class 1	Class 2	Class 3	Class 4	Class 5
< 20	20 to 50	50 to 100	100 to 500	> 500

MU from in-house validation data

Case study: **Problem description**

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Total As, *w* (mg kg^{-1})

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Target uncertainty, U^{tg} (mg kg^{-1}) [2]

Class 1	Class 2	Class 3	Class 4	Class 5
3.75 ($w > 16$)	3.75	6.25	50	50 ($w < 550$)

2. Eurachem/CITAC Guide: Setting and Using Target Uncertainty in Chemical Measurement, 2015.

MU from in-house validation data

Measurement uncertainty evaluation ❶

Precision: Intermediate precision estimated from the analysis of real sediment samples at 6.5 mg kg^{-1} and about 15 mg kg^{-1}

Trueness: Evaluated from the analysis of a Certified Reference Material

3. C. Palma et al., Talanta 192 (2019) 278-287.
4. V. Morgado et al., Analytica Chimica Acta 1175 (2021) 338732.

MU from in-house validation data

Measurement uncertainty evaluation 1

Interval I [0.05 mg kg^{-1} to 6.5 mg kg^{-1}]:

$$U^{95} = 2\sqrt{0.312^2 + (w \cdot 0.0381)^2}$$

Interval II [6.5 mg kg^{-1} to 15.4 mg kg^{-1}]:

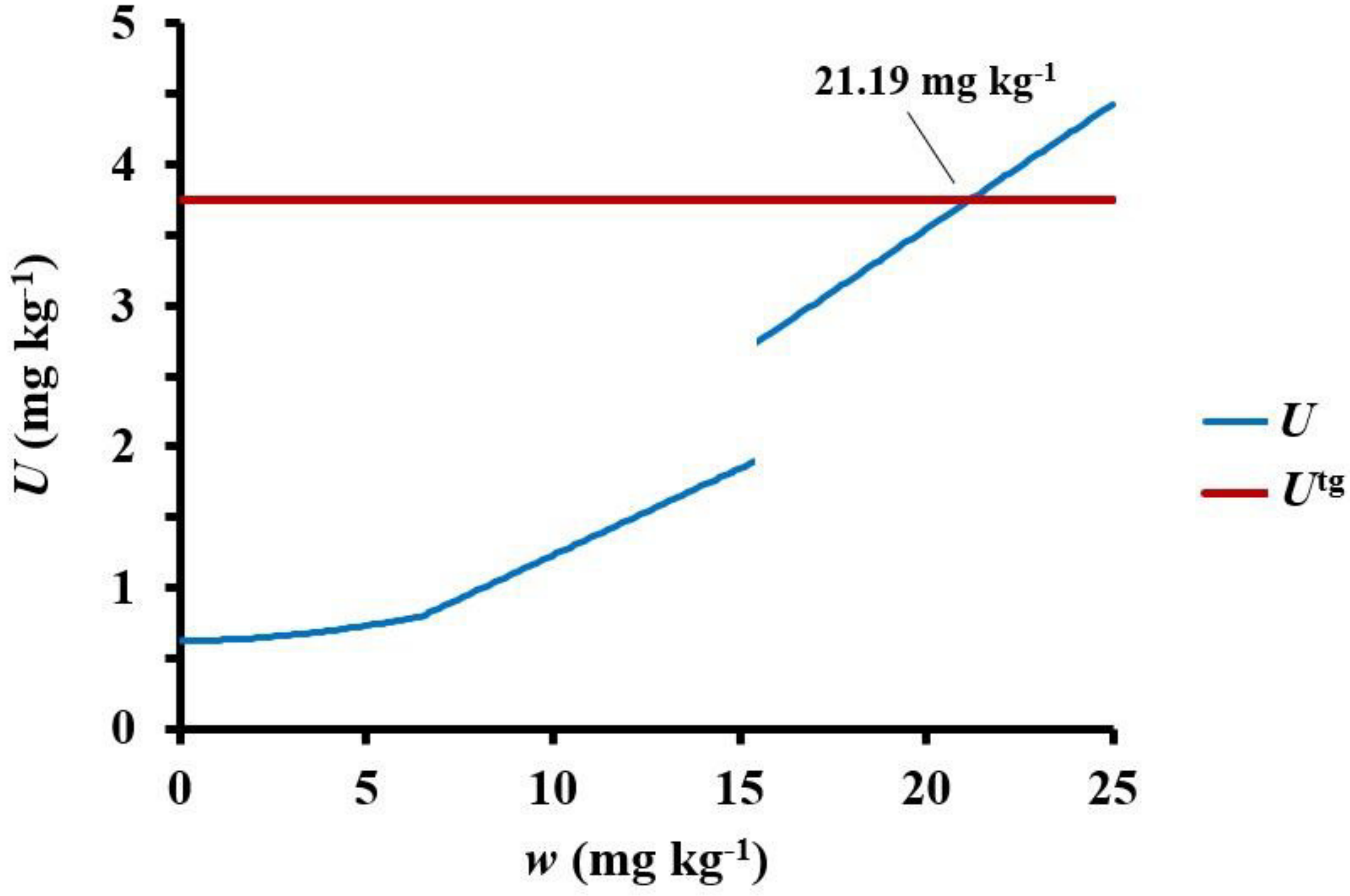
$$U^{95} = 0.123w$$

Interval III [15.4 mg kg^{-1} to 25 mg kg^{-1}]:

$$U^{95} = 0.177w$$

MU from in-house validation data

Measurement uncertainty evaluation 1

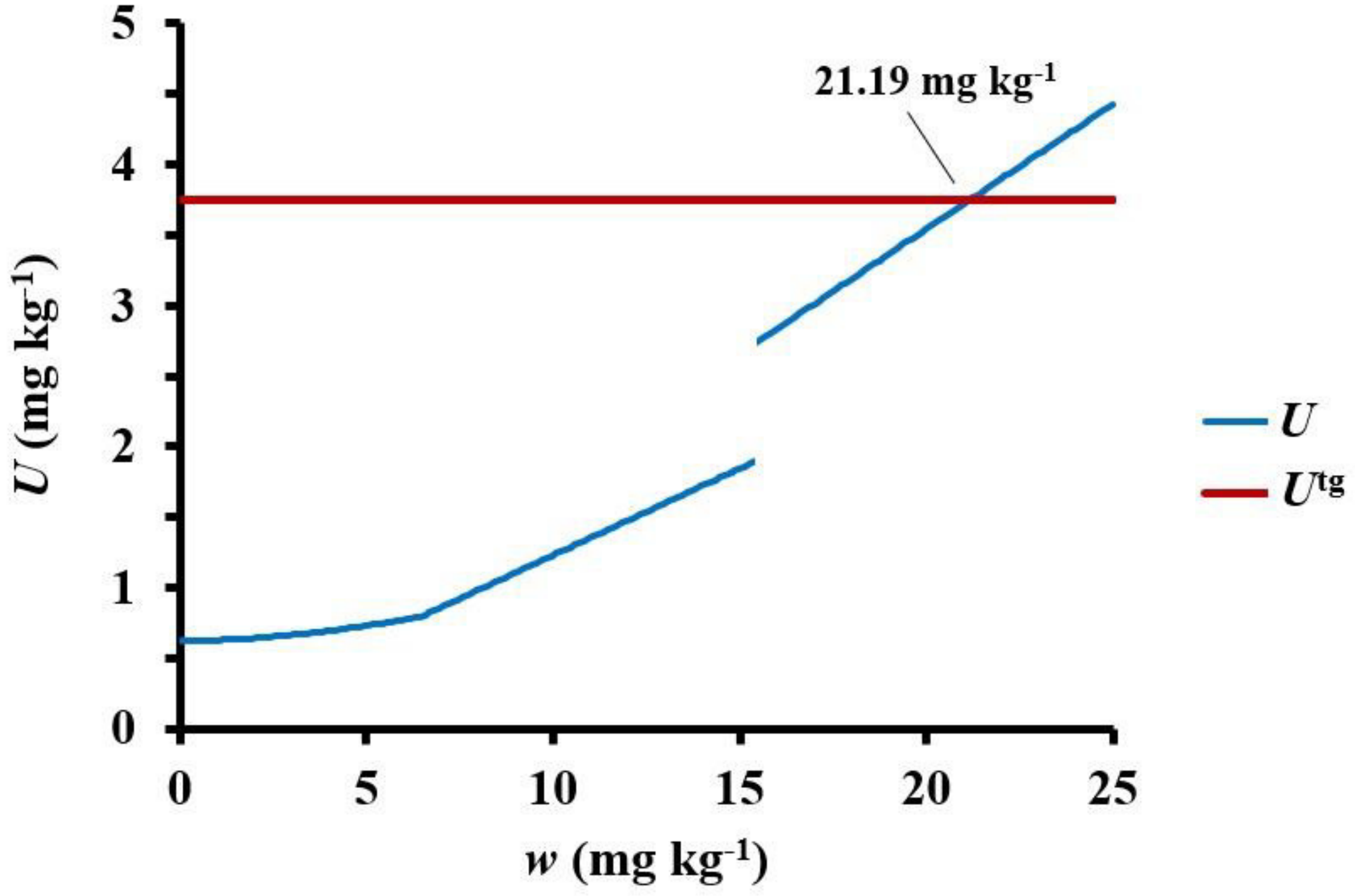


Model assumptions:

- w between 0.05 mg kg^{-1} and 25 mg kg^{-1};
- sediments not more heterogenous than analysed samples
- analysis affected by equivalent matrix effects to the observed from the analysis of the CRM.

MU from in-house validation data

Measurement uncertainty evaluation 1



MU optimisation:

Above 21.19 mg kg^{-1}, if sample is analysed twice on different days, the *U* becomes smaller than *U*^{tg}

MU from in-house validation data

Measurement uncertainty evaluation 2

Precision: Intermediate precision estimated from the analysis of real sediment samples at 6.5 mg kg^{-1} and about 15 mg kg^{-1}

Trueness: Evaluated from the analysis of a Certified Reference Material and two spiked samples with native analyte.

MU from in-house validation data

Measurement uncertainty evaluation 2

Interval I [0.05 mg kg^{-1} to 6.5 mg kg^{-1}]:

$$U^{95} = 2\sqrt{0.312^2 + (w \cdot \sout{0.03810}\ 0.0355)^2}$$

Interval II [6.5 mg kg^{-1} to 15.4 mg kg^{-1}]:

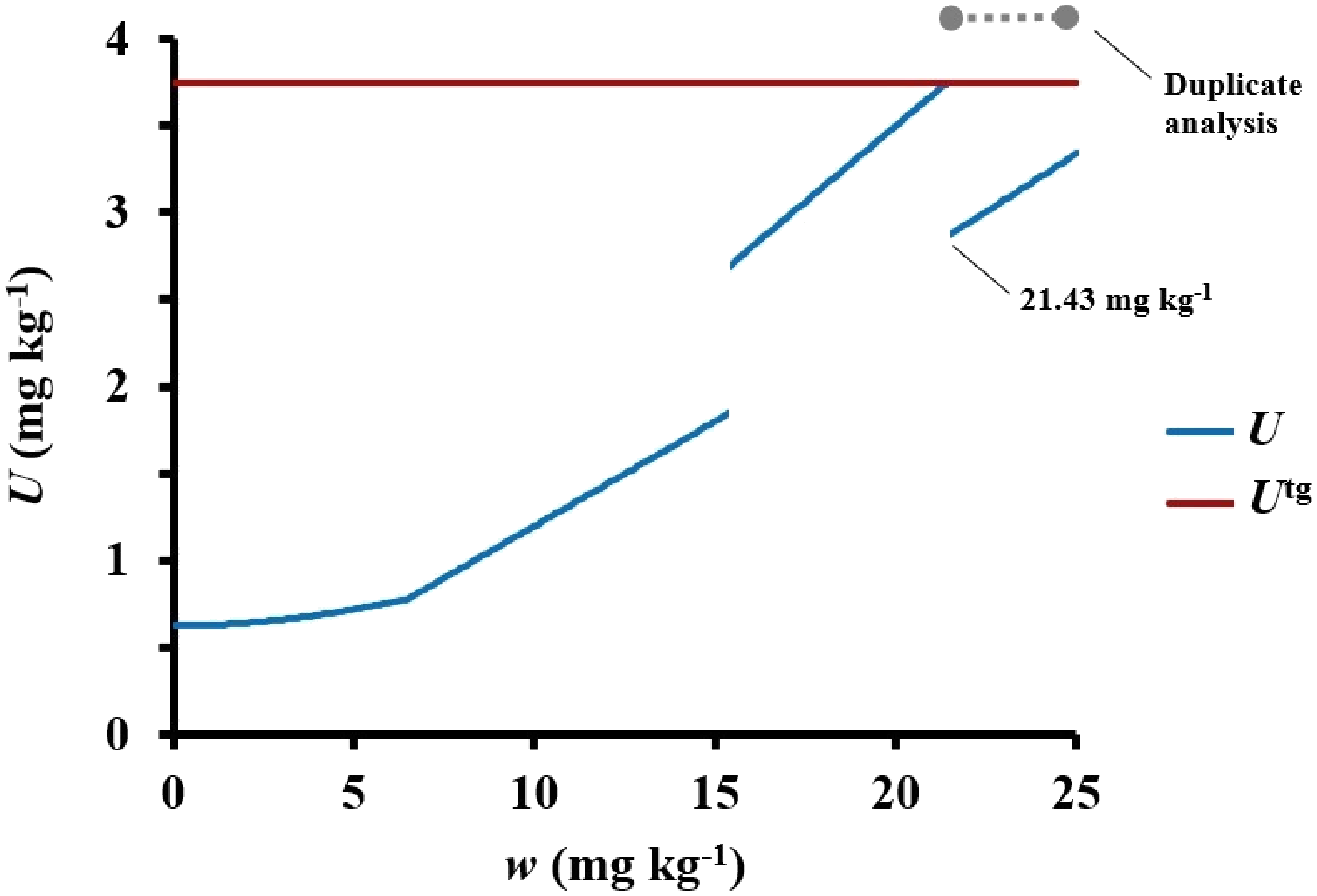
$$U^{95} = \sout{0.123}\ 0.120w$$

Interval III [15.4 mg kg^{-1} to 25 mg kg^{-1}]:

$$U^{95} = \sout{0.177}\ 0.175w$$

MU from in-house validation data

Measurement uncertainty evaluation 2



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Model assumptions:

- ***w*** **between 0.05 mg kg^{-1} and 25 mg kg^{-1};**
- **sediments not more heterogenous than analysed samples**
- **analysis affected by equivalent matrix effects to the observed from the analysis of the CRM and spiked samples**

MU from in-house validation data

Measurement uncertainty evaluation 3

Precision: (1) Samples heterogeneity from the duplicate analysis of “real” sediments; (2) Intermedia precision from the analysis of a digested stock solution;

Trueness: Evaluated from the SINGLE analysis of 22 sediment samples from proficiency tests.

MU from in-house validation data

Measurement uncertainty evaluation ❸

Interval I [0.05 mg kg^{-1} to ~~6.5~~7.5 mg kg^{-1}]:

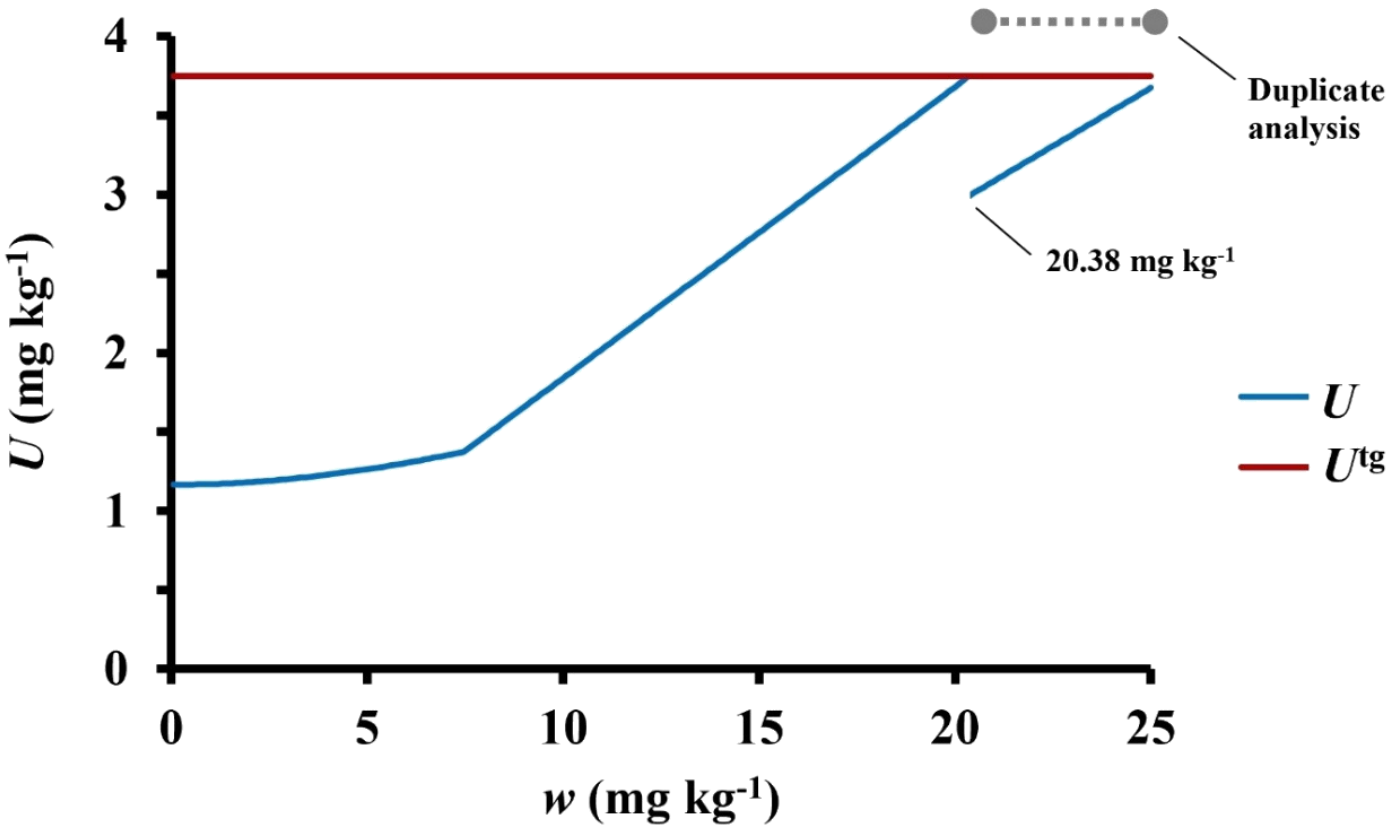
$$U^{95} = 2\sqrt{\cancel{0.312}\ 0.583^2 + (w \cdot \cancel{0.0355}\ 0.0487)^2}$$

Interval II [~~6.5~~7.5 mg kg^{-1} to ~~15.4~~25 mg kg^{-1}]:

$$U^{95} = \cancel{0.1200}\ 0.184w$$

MU from in-house validation data

Measurement uncertainty evaluation 3



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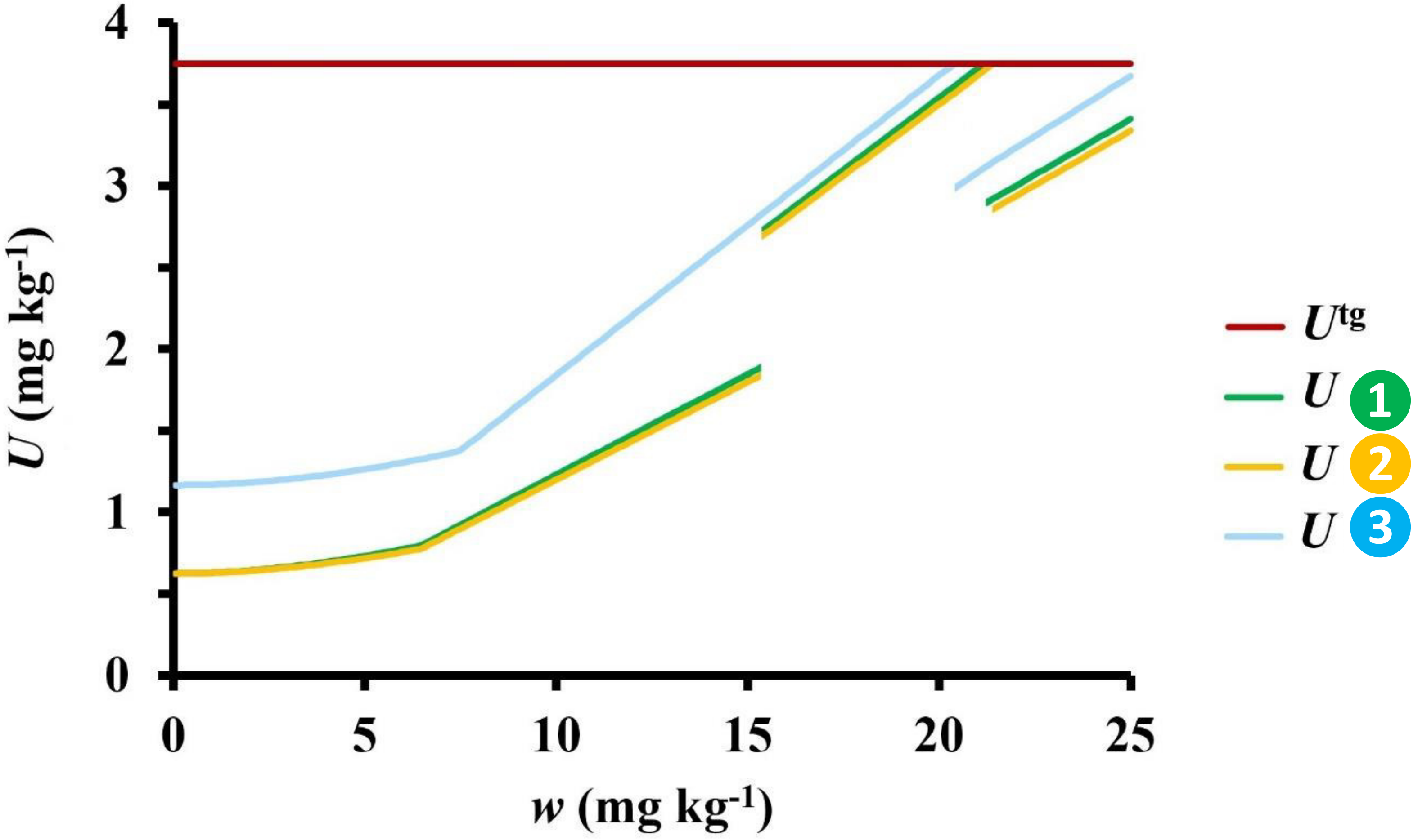
Model assumptions:

- ● *w* between 0.05 mg kg^{-1} and 25 mg kg^{-1};
- ● sediments not more heterogenous that analysed samples
- ● analysis affected by equivalent matrix effects to the observed from the analysis of the 22 proficiency test samples

MU from in-house validation data

Measurement uncertainty evaluation 1, 2 and 3



Final remarks

There is no such thing as an accurate MU evaluation:

●○● Adequate or inadequate <u>data for</u> MU evaluation

●○● Adequate or inadequate <u>use of data for</u> MU evaluation

●○● Adequate or inadequate <u>formulation of</u> MU model limitations

Final remarks

Don't be too picky with your uncertainty model

Final remarks

Don't be too picky with your uncertainty model

Thanks for your attention!