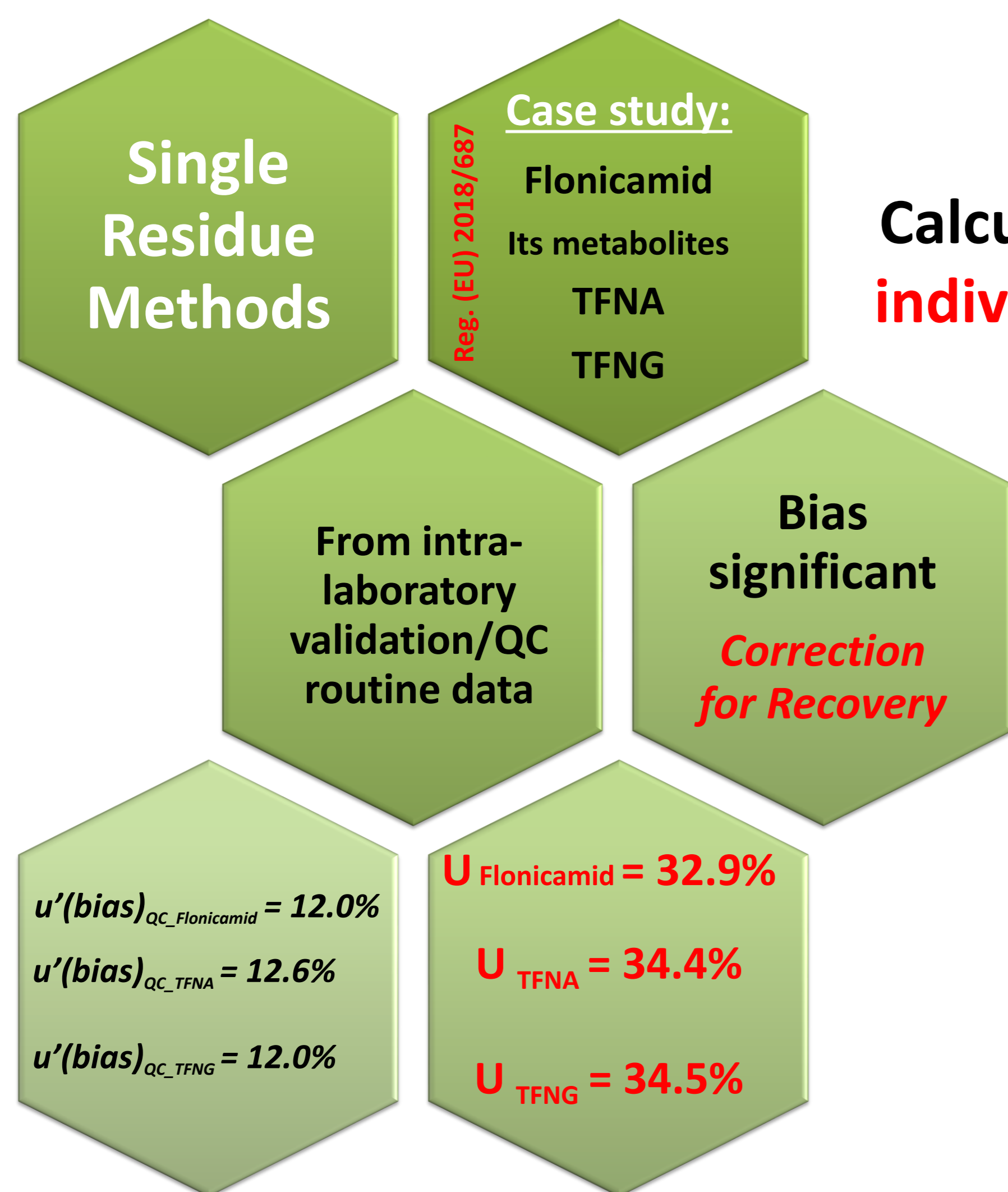


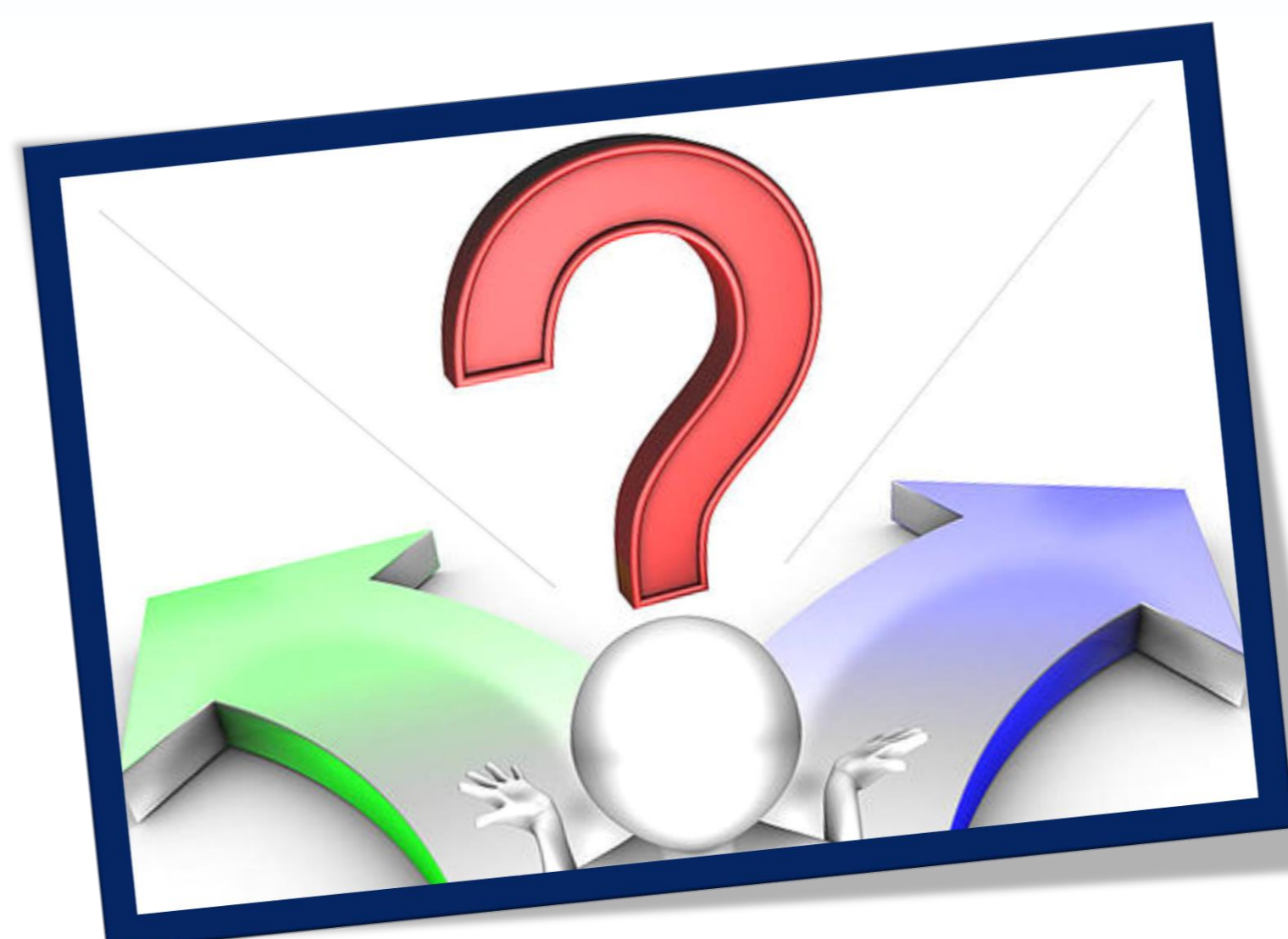
UNCERTAINTY OF MEASUREMENT AND PESTICIDE RESIDUES IN VEGETABLE PRODUCTS: APPLICATION OF ALTERNATIVE APPROACHES BASED ON QUALITY CONTROL DATA FOR MULTI/SINGLE RESIDUE METHODS

Danilo Attard Barbini, Silvana Girolimetti and Patrizia Stefanelli

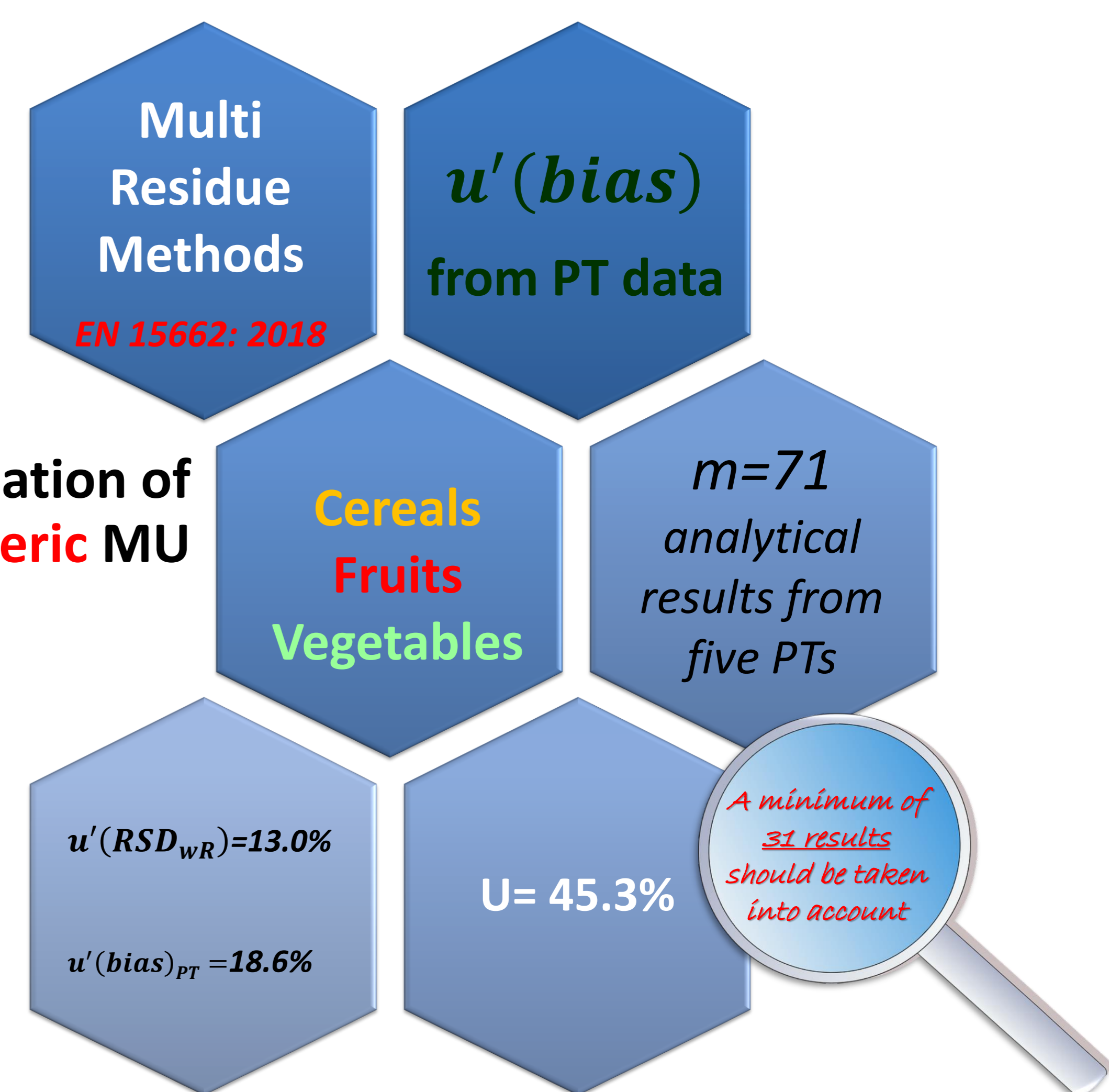
Dept. Environment and Health – National Institute of Health (Istituto Superiore di Sanità), Rome, Italy
corresponding author: patrizia.stefanelli@iss.it



Calculation of **individual MU**



Calculation of **Generic MU**



KO!

Figure 1: Assessment of Compliance with an Upper Limit

The SANTE document in order to harmonize the laboratories responsible for the official control of pesticide residues in food, recommends the use of a value (default) of 50% expanded uncertainty (coverage factor $k=2$, confidence level of 95%)

Measurement Uncertainty and Compliance with the MRL

Judgments of compliance with the MRL should comply with the criteria defined in SANTE/11813/2017: the sample is considered non-compliant if $x - U > MRL$, where x is the analytical result and U is the expanded uncertainty. (§ E12 SANTE / 11813/2017)

The use of this default value is subject to the demonstration that the expanded uncertainty of the laboratory is not more than 50%

Mean Recovery %; RSD_{WR} ($m=16$)

Fonicamid = 94%; 11%
TFNA = 91%; 12%
TFNG = 97%; 12%

Not Correction for Recovery
Good Results

$$u' = \sqrt{u'(RSD_{WR})^2 + u'(bias)^2}$$

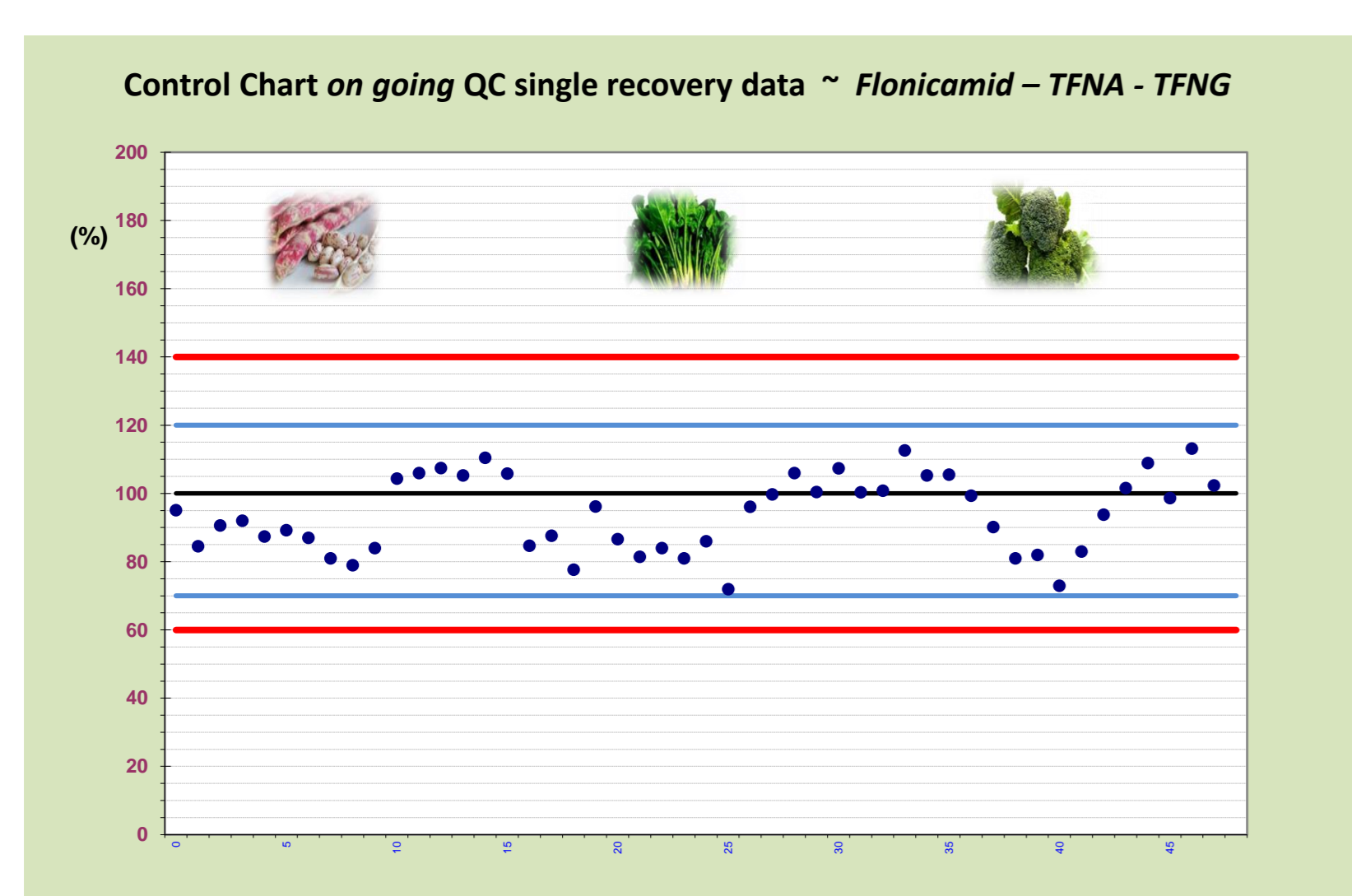
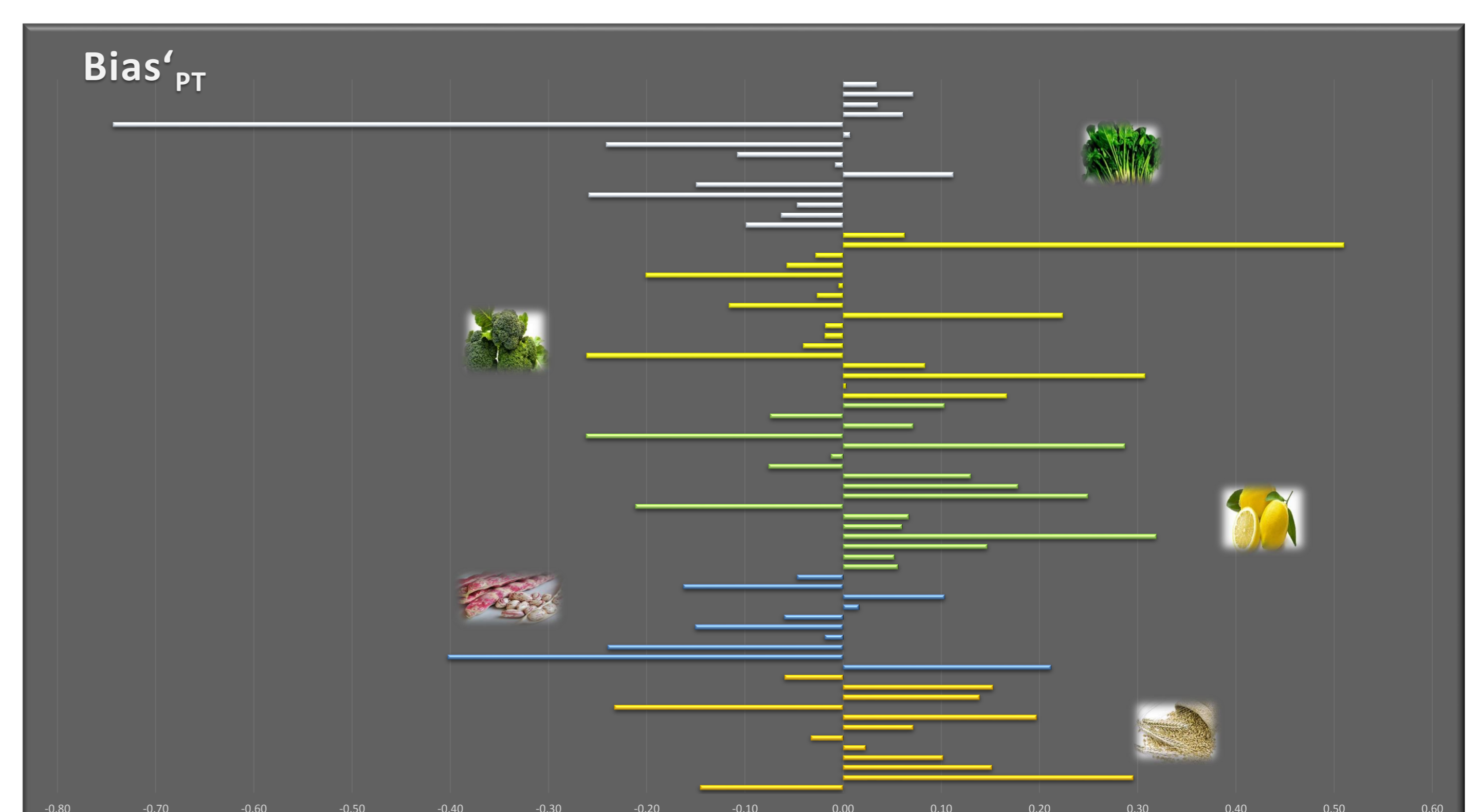
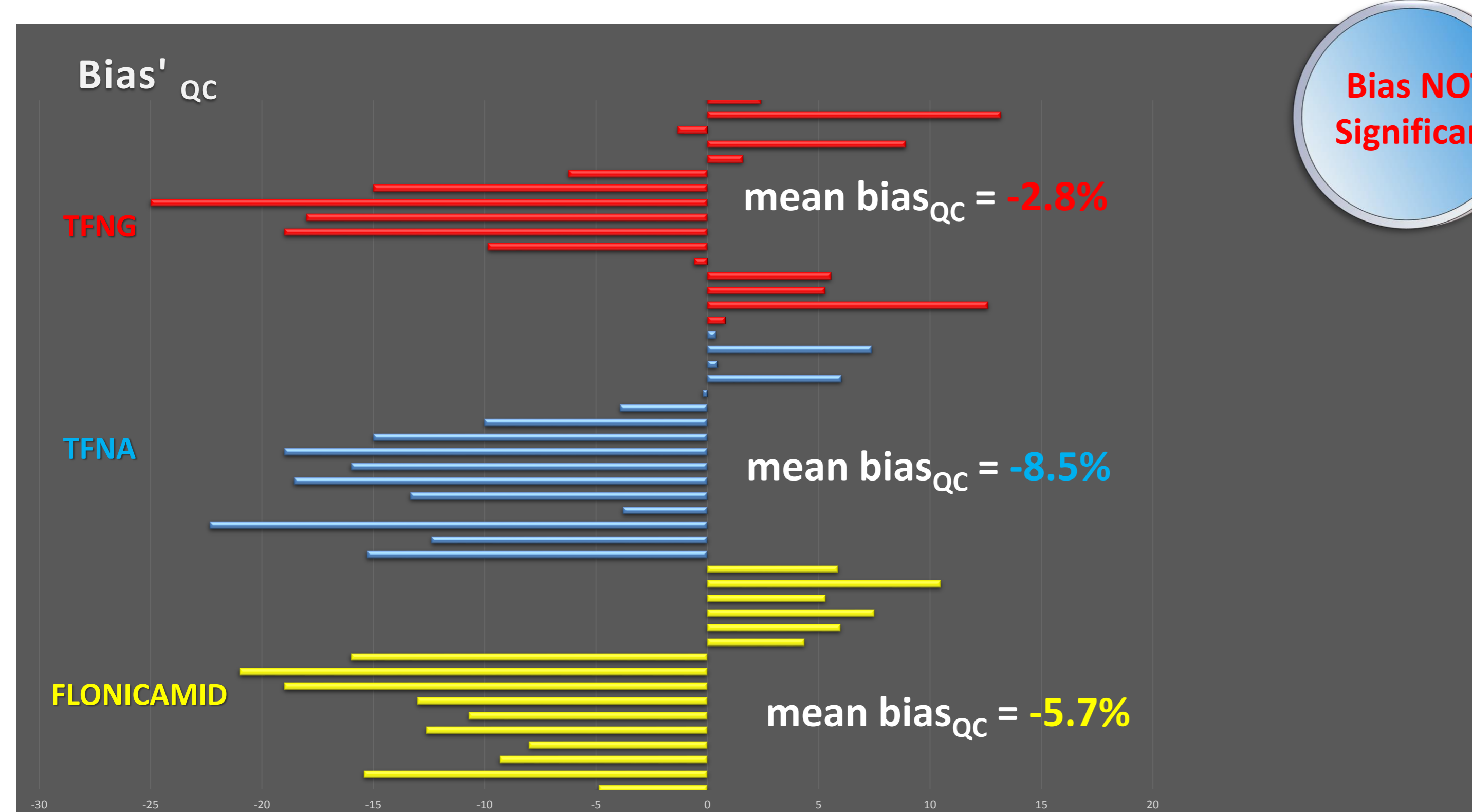
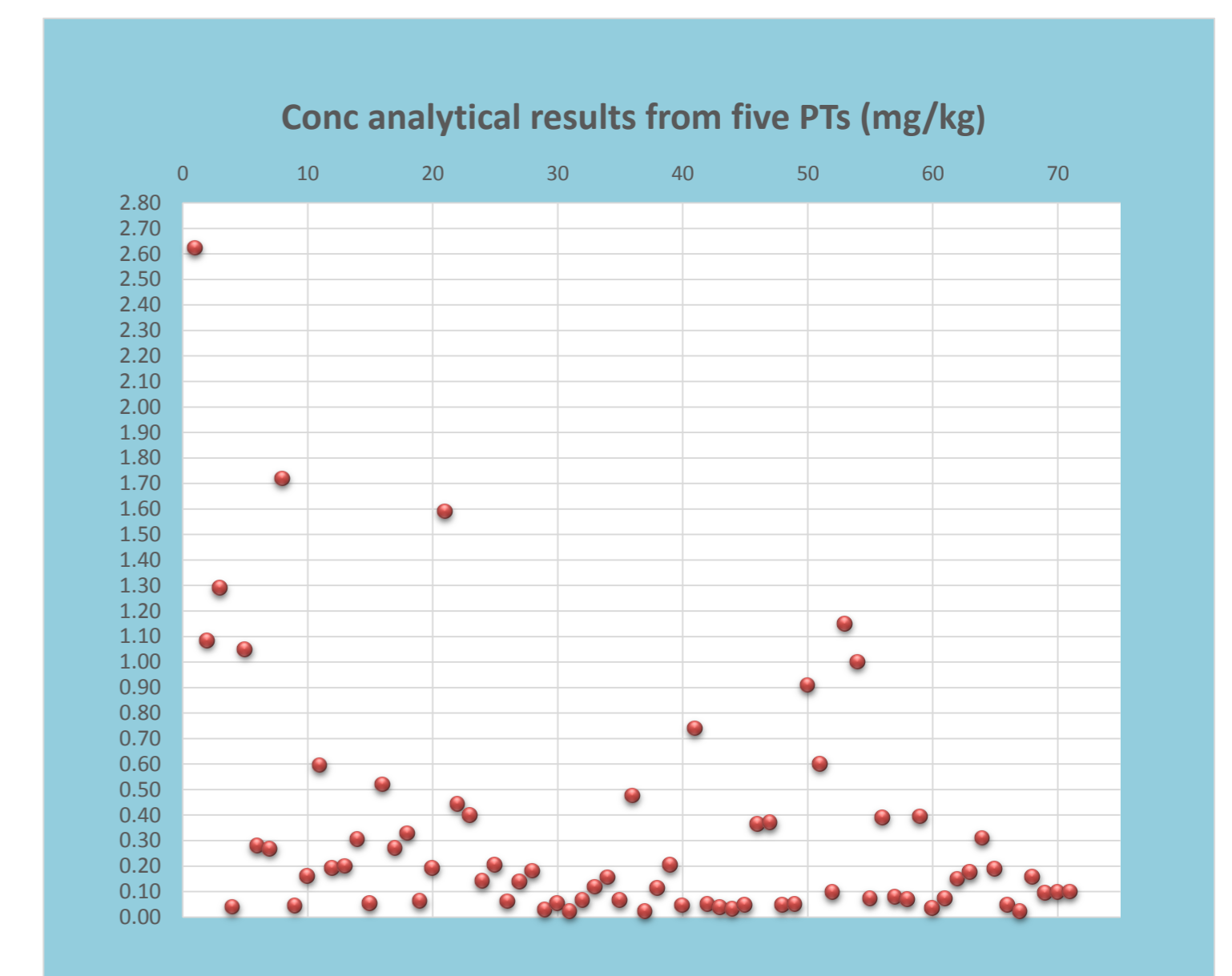
$$u'(bias)_i = \sqrt{(RMS'_{bias})^2 + u'(C_{ref})_i^2}$$

$u'(C_{ref})_{QC}$ → **NEGLIGIBLE**
Certified Reference Materials (standards) and Laboratories accredited to EN ISO/IEC 17025:2017

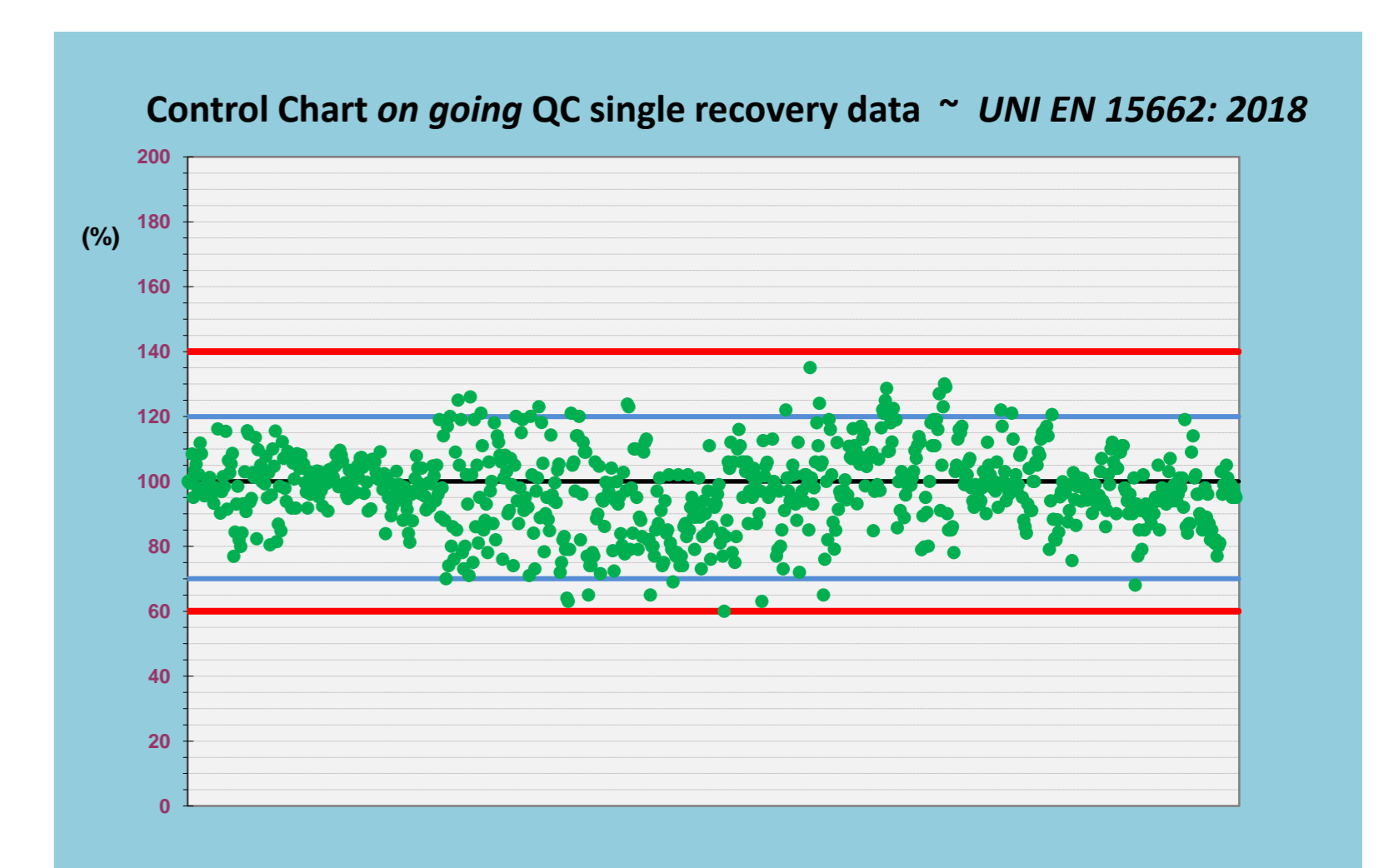
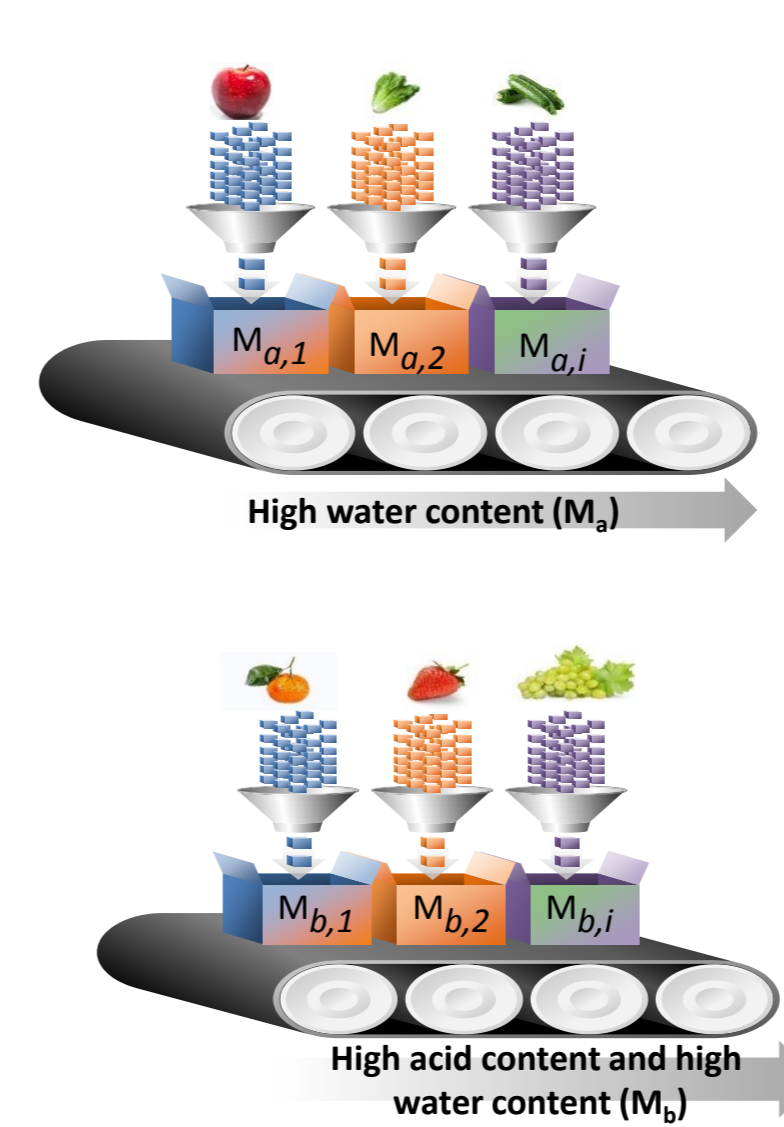
$$RMS'_{bias\ QC} = \sum \frac{bias'_{QC}}{m}$$

$$RMS'_{bias\ PT} = \sum \frac{bias'_{PT}}{m}$$

$$u'(C_{ref})_{PT} = 1.253 * \frac{\sum RSD_{PT}}{\sqrt{N}}$$



Matrices (M)	Initial Validation	On going QC
High water content (M _a)	M _{a,1}	M _{a,2} , M _{a,3} ...M _{a,i}
High acid content and high water content (M _b)	M _{b,1}	M _{b,2} , M _{b,3} ...M _{b,i}
High sugar and low water content (M _c)	M _{c,1}	M _{c,2} , M _{c,3} ...M _{c,i}
High oil content and very low water content (M _d)	M _{d,1}	M _{d,2} , M _{d,3} ...M _{d,i}
High oil content and intermediate water content (M _e)	M _{e,1}	M _{e,2} , M _{e,3} ...M _{e,i}
High starch and/or protein content and low water and fat content (M _f)	M _{f,1}	M _{f,2} , M _{f,3} ...M _{f,i}



References

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European Committee for Standardization. Foods of plant origin – Multimethod for the determination of pesticide residues using GC- and LC- based analysis following acetonitrile extraction/partitioning and clean-up by dispersive SPE – Modular QuEChERS method. EN 15662:2018

Workshop Eurachem/Eurolab Workshop
Uncertainty from sampling and analysis for accredited laboratories
Berlin the 19th - 20th November 2019