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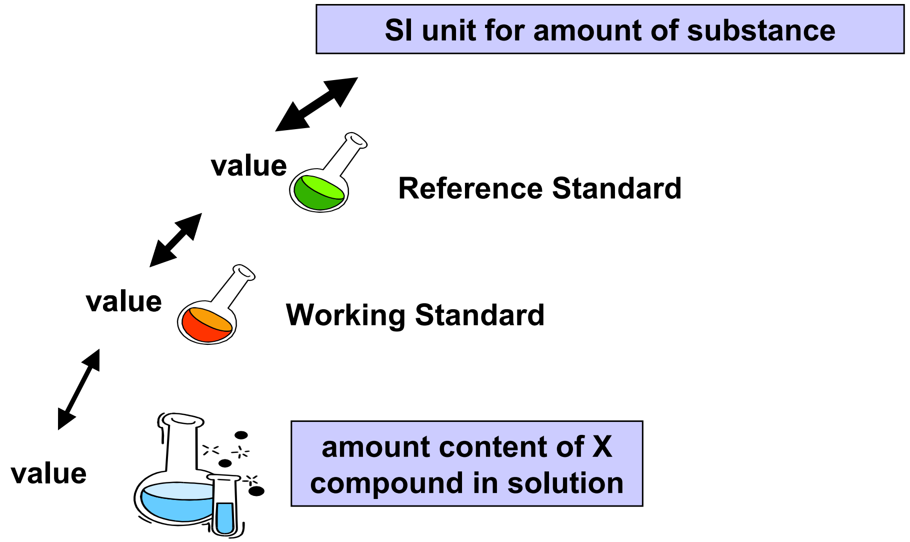
Requirements for comparable mercury speciation analyses in seawater

Analytical measurements need to be comparable in time and space **Traceability** is the best way to achieve this

Traceability

“ ... the property of the **result of a measurement** or the value of a standard whereby it can be related to **stated references**, usually national or international standards, through an **unbroken chain of comparisons** all having **stated uncertainties**.”

Traceability of Chemical Measurements



(Papadakis, 2000)

Measurement uncertainty

How to calculate uncertainty (u)?

Measurement uncertainty

- ISO-GUM approach (bottom-up)
- Uncertainty contributions (x_i)

- Matematical model
- Additional sources

$$u_c^2(y) = \sum_{i=1}^{N} \left[c_i u(x_i) \right]^2 \equiv \sum_{i=1}^{N} u_i^2(y)$$

$$u_c^2(y) = \sum_{i=1}^{N} \left(\frac{\partial f}{\partial x_i} \right)^2 u^2(x_i)$$

Comparison of the results from two methods

Determination of MeHg in seawater

Analysis performed by two different analytical methods

Method 1
(Ethylation/CV AFS)

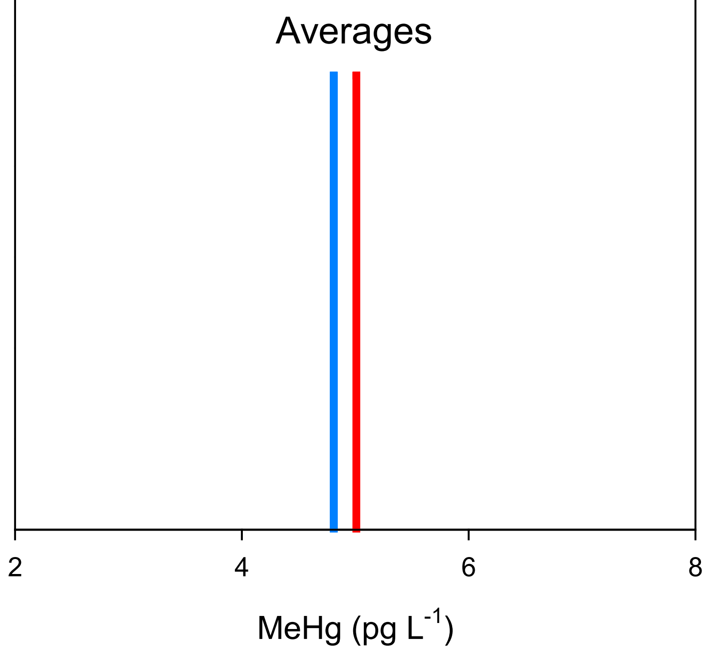
c (MeHg) = 4.81 pg/L

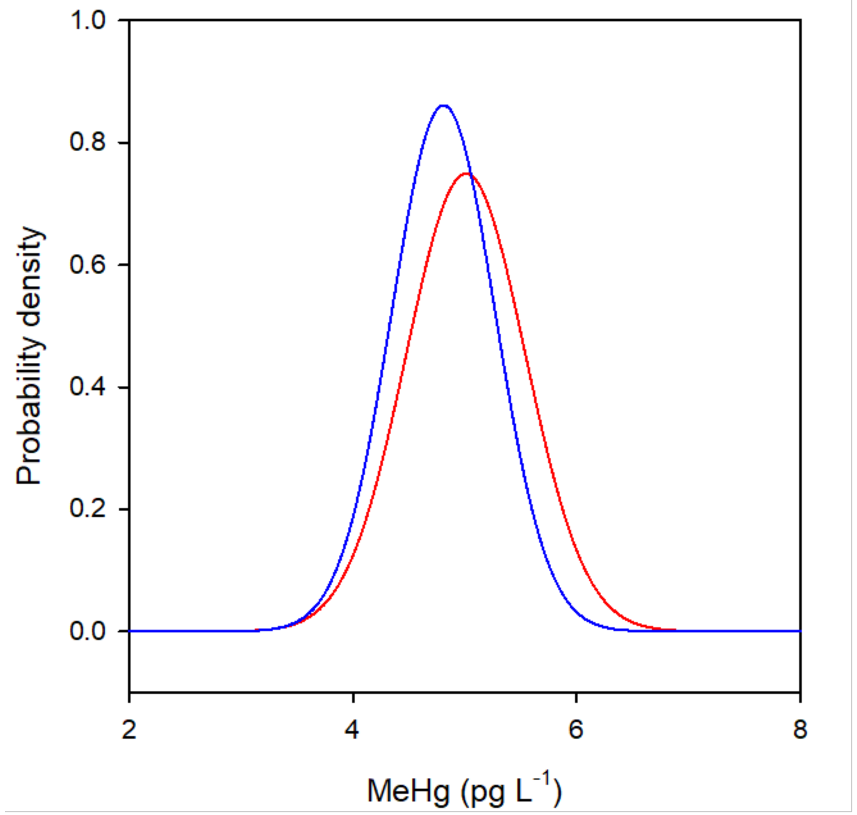
Method 2
(Hydration/CV AFS)

c (MeHg) = 5.01 pg/L

Are these measurement results the same?

Let’s compare results

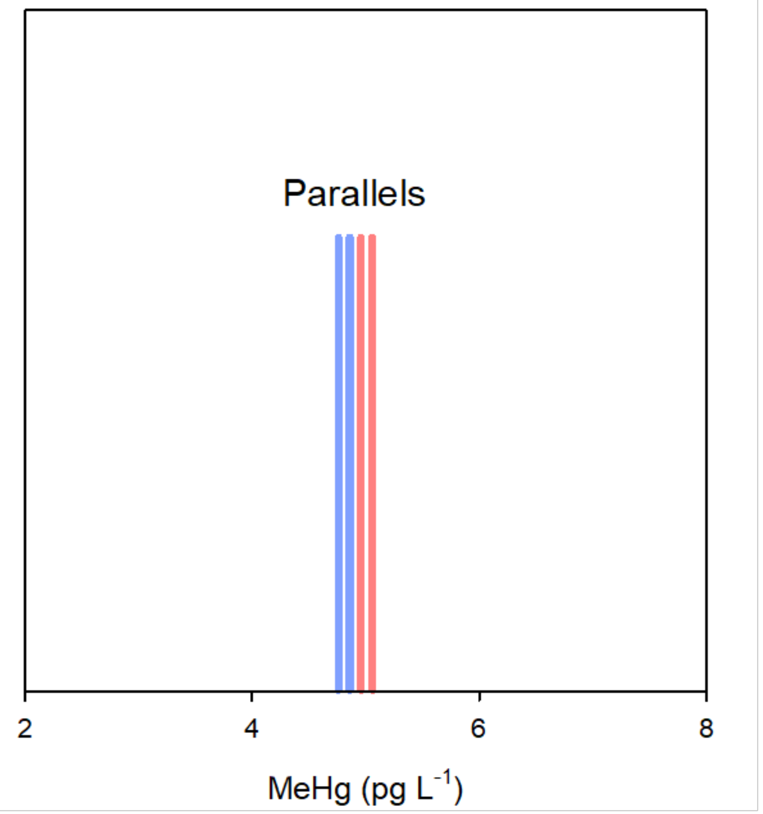




All **uncertainty** sources are taken into an account

Comparison of distributions

Only repeatability is taken into an account



Analytical methods for Hg speciation analysis in seawater

- THg – US EPA method 1631
- DGM – purge and trap, double amalgamation, CVAFS
- MeHg – extraction, ethylation, preconcentration, CVAFS
- MeHg – hydride generation, preconcentration, CVAFS

Fraction	Concentration level (pg L^{-1})	$U_{r,c}$ (%) (k = 2)
THg	200 – 300	23.6
	400 – 500	16.8
	600 – 800	12.0
	1000 – 2000	9.56
DGM	20 – 40	21.9
	80 – 100	15.7
	150 – 300	13.2
MeHg (hydride generation)	< 10	21.3
	20 – 30	15.0
	> 80	11.1
MeHg (ethylation)	< 10	19.3
	20 – 30	18.2
	> 80	15.8

Measurement uncertainty

- The greatest confidence in the highest concentrations with the lowest uncertainty
- Knowing the complete procedure
- Determine the most important contributions

Strategy for proper sampling planning

Planning a long-term monitoring of Hg in sea water to observe differences in speciation due to environmental stressors

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Relations between mercury fractions and microbial community components in seawater under the presence and absence of probable phosphorus limitation conditions

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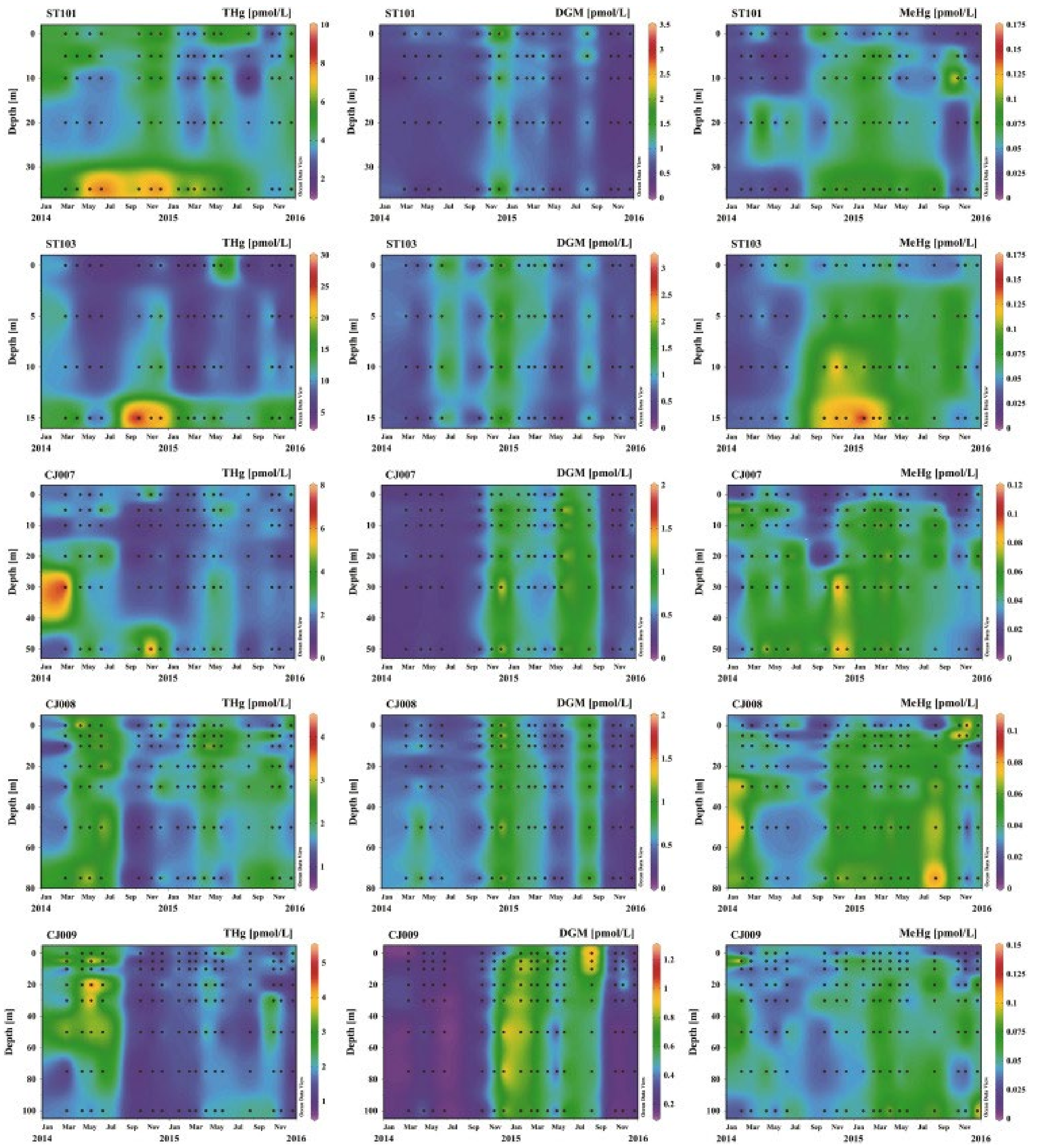
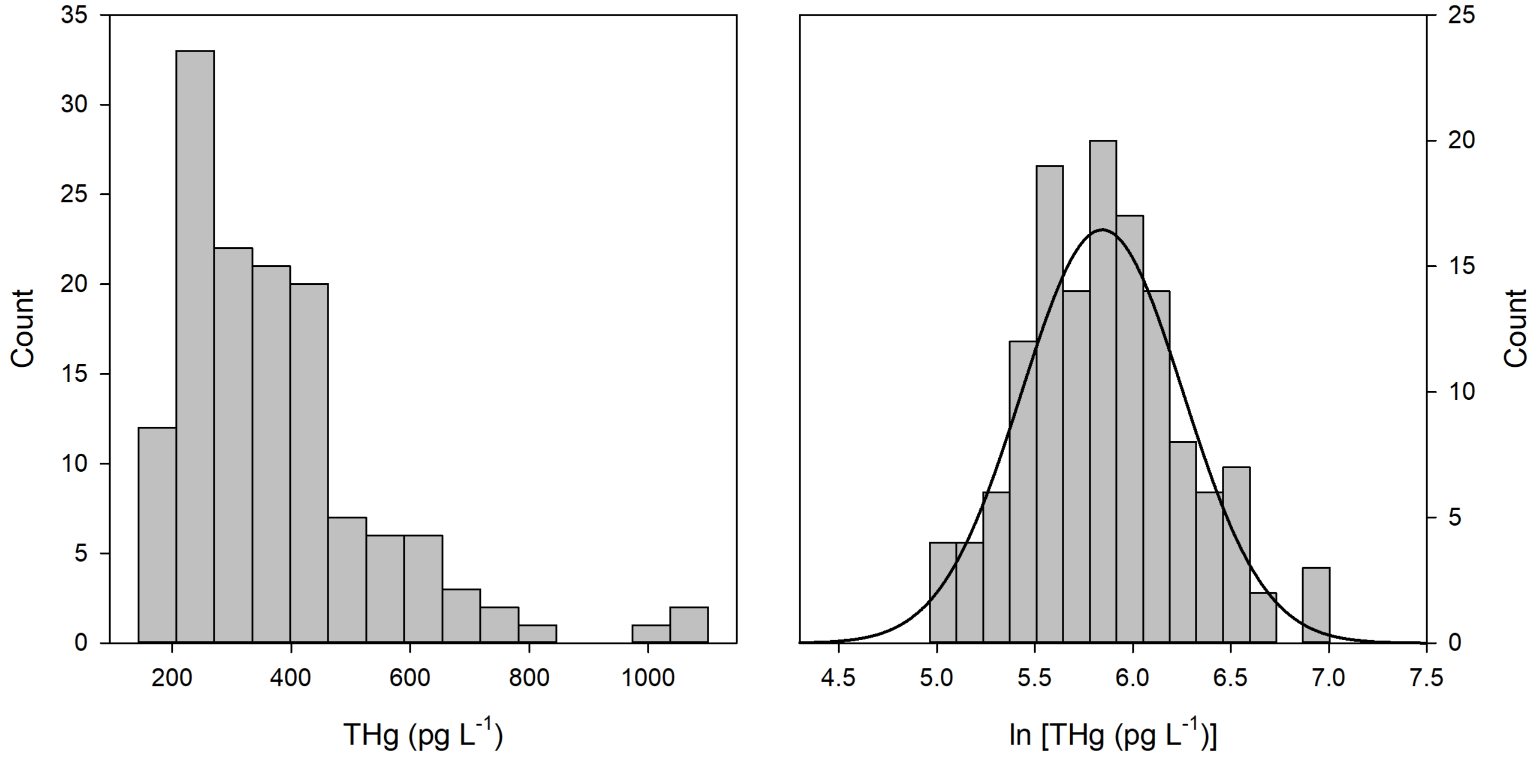


Strategy for proper sampling planning

Proper application of statistical tests for data interpretation and comparability

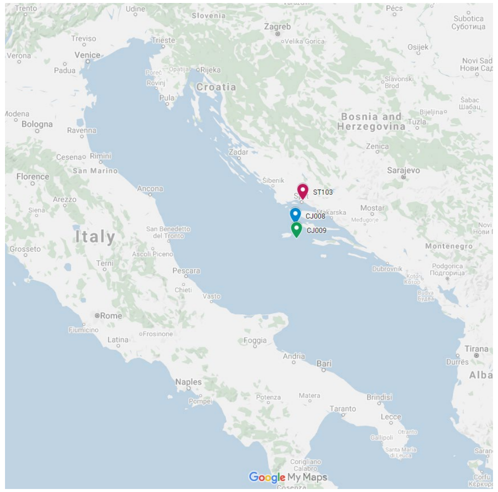
- Statistical methods
  - Check data normality
- Data transformations
  - Linear scale
  - Log-scale



How to avoid reporting 0.40 ± 0.60 ng L^{-1}?

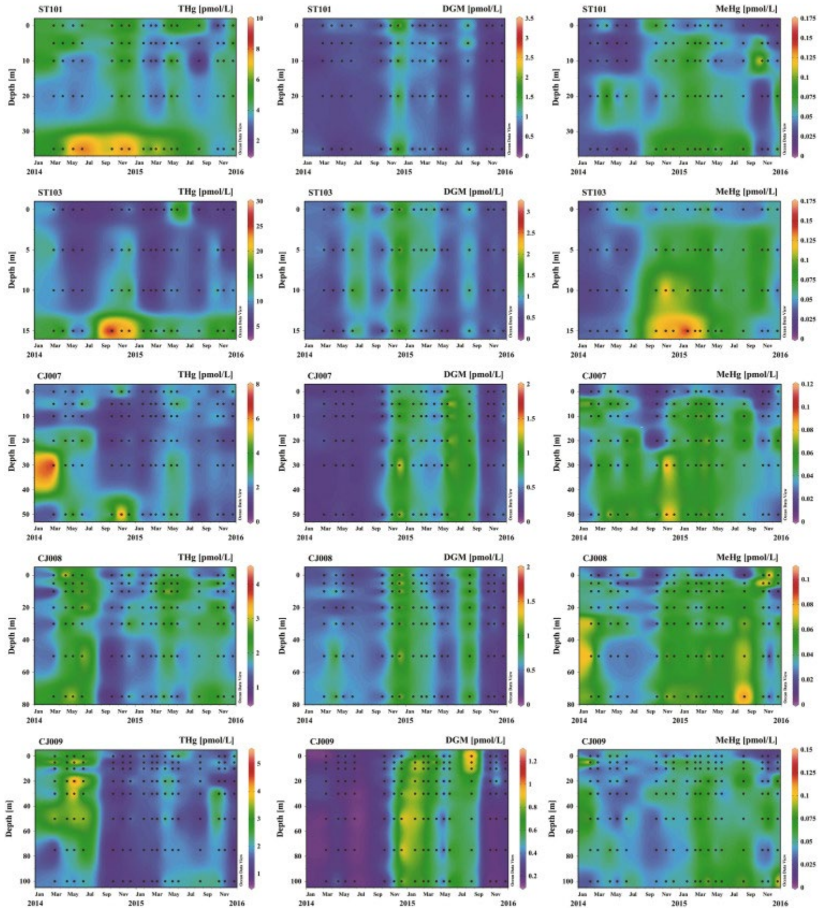
Geometric mean (GM) of 0.33 ng L^{-1} with 95% CI from 0.14—0.80 ng L^{-1}

Statistics on log-scale



Strategy for proper sampling planning

What is the natural variability of THg, MeHg, and DGM in seawater? - Central Adriatic Sea



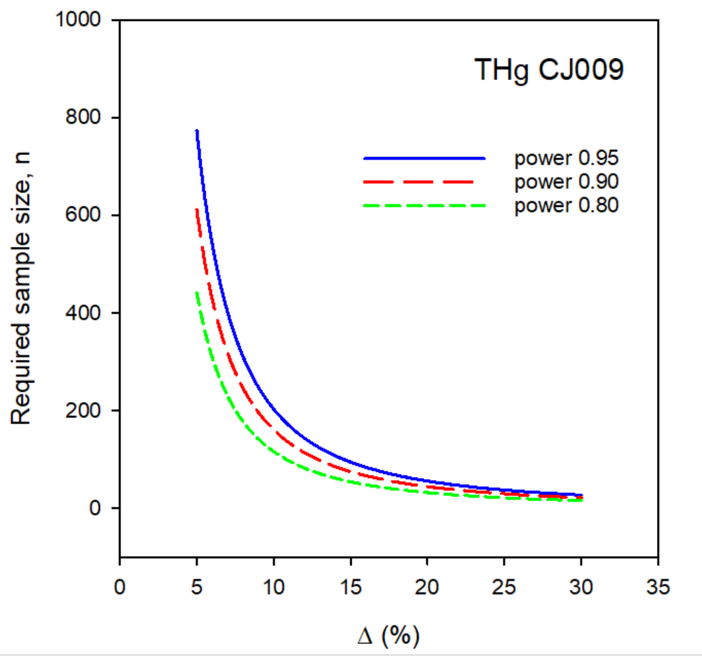
Analyte	Station	n	Min – Max (pg/L)	GM (GSD) (pg/L)	95% CI (pg/L)
THg	All	323	108 – 5575	492 (2.20)	102 – 2377
	ST103	68	693 – 5575	1783 (1.65)	655 – 4850
	CJ008	119	108 – 834	354 (1.46)	165 – 759
	CJ009	136	143 – 1101	345 (1.51)	151 – 787
DGM	All	323	19.9 – 606	89.1 (2.10)	20.1 – 394
	ST103	68	31.8 – 606	142 (1.92)	38.3 – 523
	CJ008	119	21.6 – 393	91.7 (1.94)	24.2 – 347
	CJ009	136	19.9 – 245	68.9 (2.09)	15.7 – 302
MeHg	All	323	1.28 – 34.3	8.90 (1.66)	3.21 – 24.7
	ST103	68	2.21 – 34.3	11.8 (1.75)	3.82 – 36.3
	CJ008	119	1.28 – 20.7	7.41 (1.67)	2.65 – 20.7
	CJ009	136	2.56 – 22.2	9.09 (1.50)	4.06 – 20.4

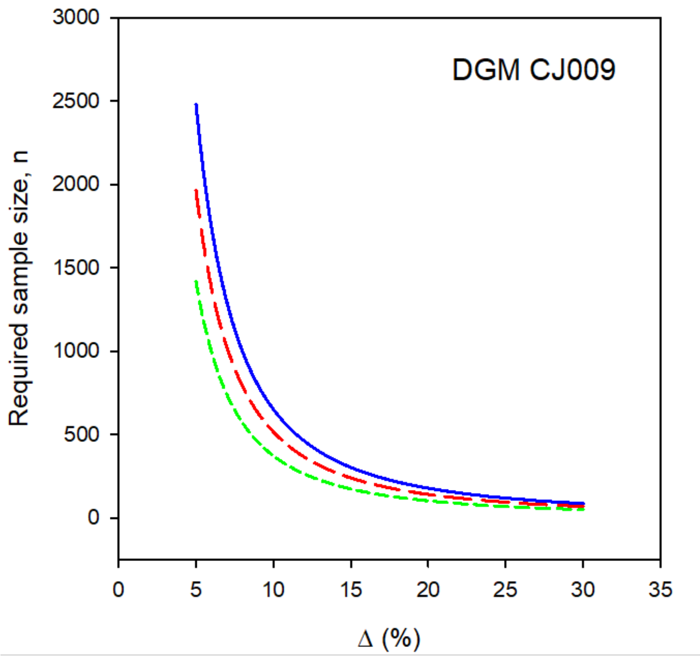
Sample size determination

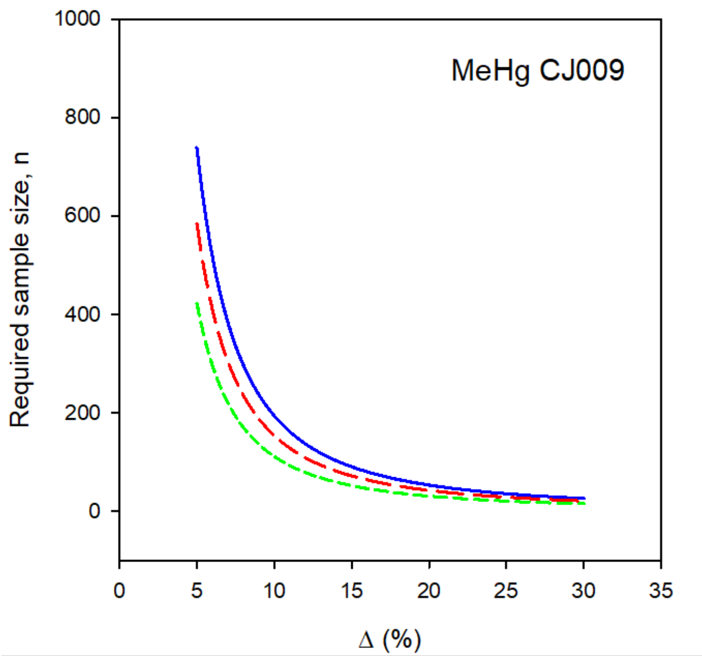
GM vs. postulated value

- **Only natural sample variability**
- Analysis performed on log-scale

- Sample size (n)
- Station CJ009 (open sea)
- Δ – expected difference in GM
- Three statistical powers
- One-sided t-test
- α value of 0.05







What about the influence of measurement uncertainty?
Measurement uncertainty – normal distribution on linear scale
Natural variability – normal distribution on log-scale

Conversion of uncertanty from **linear to log** scale is possible

Conversion of data variability (natural) from **log to linear** scale is usually not possible

Determination of sample size should be performed on log-scale

We show here that the log-normal distribution can be well approximated by the normal distribution when the relative standard uncertainty is small. Let us consider a random quantity X which follows the log-normal distribution with parameters η and σ^2. If we name $f_X(X)$ the distribution of X we have

$$f_X(X) = \frac{1}{\sqrt{2\pi}\sigma X} e^{-\frac{[\ln(X)-\eta]^2}{2\sigma^2}} \qquad (A.1)$$

where we have assumed, for simplicity, the linear-to-log transformation $Y = \ln(X)$, where 'ln' is the natural logarithm. The parameters of the log-normal distribution can be linked to the expected value of X, $E\{X\}$, and the variance of X, $\text{Var}\{X\}$ as follows [4, invert equations (4) and (5)]

$$\eta = \ln(E\{X\}) - \frac{1}{2}\ln\left(1 + \frac{\text{Var}\{X\}}{E^2(X)}\right) \qquad (A.2)$$

$$\sigma^2 = \ln\left(1 + \frac{\text{Var}\{X\}}{E^2\{X\}}\right) \qquad (A.3)$$

Since the relative standard uncertainty of X is small, we have $\sqrt{\text{Var}\{X\}}/E\{X\} \ll 1$, then

$$\eta \approx \ln(E\{X\}) - \frac{1}{2}\frac{\text{Var}\{X\}}{E^2(X)} \qquad (A.4)$$

$$\sigma^2 \approx \frac{\text{Var}\{X\}}{E^2\{X\}} \qquad (A.5)$$

Substituting (A.4) and (A.5) into (A.1) we obtain, after manipulation,

$$f_X(X) \approx \frac{1}{\sqrt{2\pi \text{Var}\{X\}}} \frac{E\{X\}}{X} e^{-\frac{\left[\ln\left(1+\frac{X-E\{X\}}{E\{X\}}\right)+\frac{1}{2}\frac{\text{Var}\{X\}}{E^2\{X\}}\right]^2}{2\frac{\text{Var}\{X\}}{E^2\{X\}}}} \qquad (A.6)$$

The multiplying term $E\{X\}/X$ at the right-side of can be safely approximated by 1 and the logarithm in the argument of the exponential by $(X - E\{X\})/E\{X\}$. Further, taking into account that $1/2(\text{Var}\{X\}/E^2\{X\}) \ll |X - E\{X\}|/E\{X\}$ and rearranging we have from (A.6)

$$f_X(X) \approx \frac{1}{\sqrt{2\pi \text{Var}\{X\}}} e^{-\frac{(X-E\{X\})^2}{2\text{Var}\{X\}}} \qquad (A.7)$$

which is the normal distribution having expected value $E\{X\}$ and standard deviation $\sqrt{\text{Var}\{X\}}$. Note that, when the relative dispersion is low, $E\{X\}$ is accurately estimated by both the arithmetic and geometric mean, and $\sqrt{\text{Var}\{X\}}$ by the standard deviation and by $x_g[u_g(X) - 1]$, where x_g is the geometric mean and $u_g(X)$ is the geometric standard deviation as given by (3) and (6), respectively.

(Carobbi, 2010: The Use of Logarithmic Units in the Uncertainty Evaluations of EMC Measurements; IEEE)

Sample size determination

Example for CJ009; GM vs. postulated value: **5% difference**; statistical power 0.95, α = 0.05

	Sample variability	Sample variability + uncertainty
THg	773	805
DGM	2483	2511
MeHg	739	781

Example for CJ009; GM vs. postulated value: **20% difference**; statistical power 0.95, α = 0.05

	Sample variability	Sample variability + uncertainty
THg	56	58
DGM	178	180
MeHg	53	56

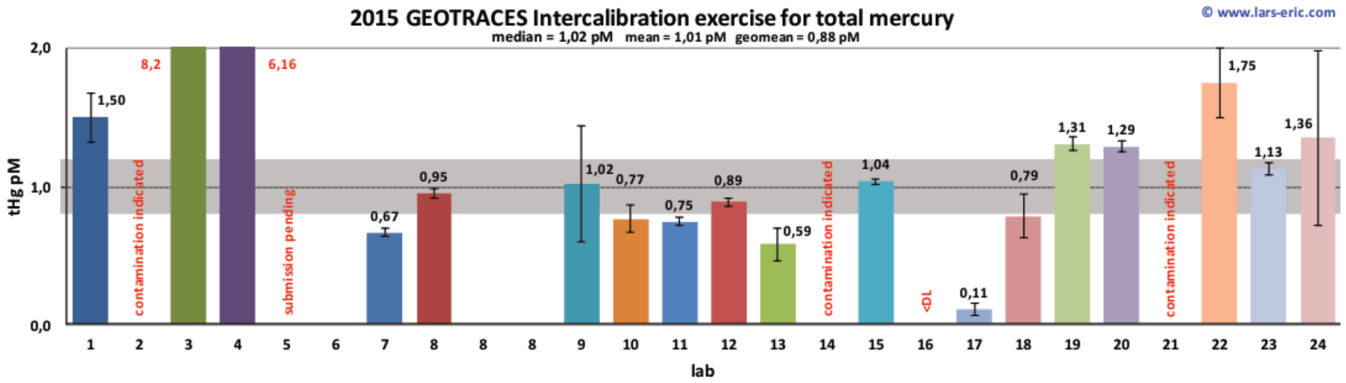
Strategy for proper sampling planning

What is the influence of different results obtained by various laboratories?

Interlaboratory comparisons:

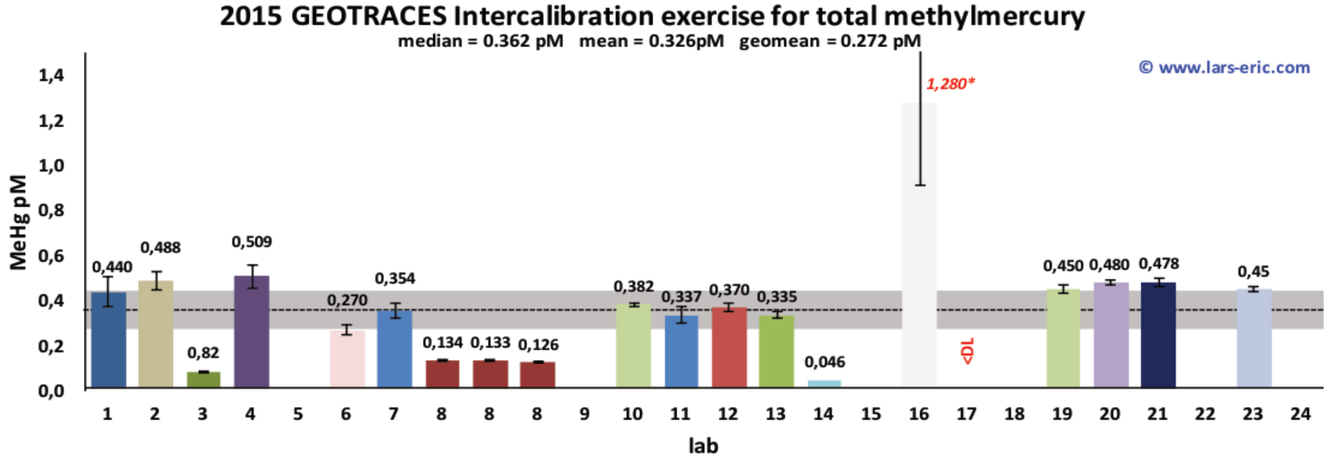
Variability between methods/laboratories

Planning of the interlaboratory comparisons
ISO 17 043
ISO/REMCO standardi



median = 1,02 ± 0,31 pM; min = 0,11 pM; max = 1,75 pM; RSD = 30%

9 measurements within 20% precision band (grey)



median = 0,362 ± 0,129 pM; min = 0,046 pM; max = 0,509 pM; RSD = 39 %

13 measurements within 20% precision band (grey)

(Heimburger-Boavida et al., 2015)

Sample size determination

Example for CJ009; GM vs. postulated value: **5% difference**; statistical power 0.95, α = 0.05

	Sample variability	Sample variability + uncertainty	**Sample variability + uncertainty + interlab comparison**
THg	773	805	**850**
DGM	2483	2511	**2779**
MeHg	739	781	**832**

Example for CJ009; GM vs. postulated value: **20% difference**; statistical power 0.95, α = 0.05

	Sample variability	Sample variability + uncertainty	**Sample variability + uncertainty + interlab comparison**
THg	56	58	**61**
DGM	178	180	**200**
MeHg	53	56	**60**

Few things to think about…

- Importance of measurement uncertainty
- Metrological treaceability
- Individual data alone are not enough for data comparison
- Data variability is important for proper interpretation and study design
- Uncertainty and not only SD from small number of measurements
  - Data not comparable and/or trustworthy, measurement uncertainty has to be taken into an account
- Intelaboratory comparison for comparison of models
  - Determination of spatial and time trend
  - Interpretation of data for models for future trends