Calculating QA bias and variability from laboratory comparisons

Currently implemented for inorganic (main) compounds, heavy metals and EC/OC, for which centralised annual laboratory comparison are conducted.

Laboratory intercomparisons have been conducted in EMEP almost since the start of the program, and it has been a very important tool to assess and improve the quality of the measurements. The results from these round-robin tests were up to 2016 only available in separate reports and not directly linked to the data in the database. The introduction of QA measures in the data submission format has changed this.

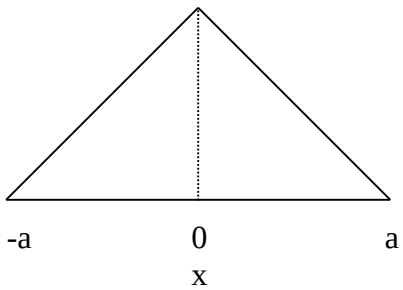
To compare results from the intercomparison in the network, both in time and space, and across components, it is necessary that the calculations are done in a centralized and harmonized way. EMEP/CCC will therefore, based on the results of systematic and random errors in the different intercomparisons, provide information which directly can be included in the nasa ames files for the annual data reporting. It is recommended to use results from the two consecutive intercomparisons, which both represents part of the year the measurements are done. The results can be found here: http://www.nilu.no/projects/ccc/intercomparison/qameasure/

QA metadata are split into QA variability and QA bias. The QA variability can be linked up to the data quality objectives (DQO) if these have been defined, to determine whether the lab has passed or not passed the QA measure. The QA bias is signed with systematic if more than 75% of the samples in the comparison are systematic negative or positive, giving a possibility for the data user to correct the data if wanted.

The statistical background for how the QA variability and bias have been calculated:

Calculation of QA variability = Random errors (2RSD)

It is assumed that laboratories taking part in comparisons will obtain results near the expected ones when this bias is removed, and that the differences between expected and obtained results more often will be close to zero than not. Based upon this assumption, a triangular distribution can be used to quantify the random errors in the laboratory results (Eurachem, 2000; EMEP CCC report 6/2003).



The triangle distribution is symmetric with a baseline 2a. The height in the triangle will be 1/a when the triangle area equals 1. The standard uncertainty is given by

$$u(x) = \frac{a}{\sqrt{6}} \qquad (1)$$

The distance from –a to a (i.e. 2a) is called the range. When applied on the laboratory comparison results, the range equals the distance between the largest and smallest of the differences between expected and found concentrations. L and T represent the laboratories' and the expected concentrations respectively, and D is the difference:

$$D_i = L_i - T_i \tag{2}$$

The range (2a) is then the difference between the highest and minimum differences ($D_{max} - D_{min}$) and the uncertainty $u(D)$, for the differences becomes

$$u(D) = \frac{\left(D_{\max} - D_{\min}\right)}{\left(2 \cdot \sqrt{6}\right)}. \tag{3}$$

and more than 95 % of the data will be within $\pm 2 \cdot u(D)$. The QA variability is defined as the relative standard deviation (RSD) given by the 95% confidence limit, thus:

$$\text{QA variability} \quad = \quad 2 \cdot RSD = \frac{2 \cdot u(D) \cdot 100}{\frac{\sum_{i=1}^{n} T_i}{n}} \% = \frac{n \cdot (D_{\max} - D_{\min})}{\sqrt{6} \cdot \sum_{i=1}^{n} T_i} \% \tag{4}$$

Calculating the QA bias = systematic error (RB%)

An estimation of bias in single measurements requires a long data series, and only a few samples in a laboratory comparison will only give a very coarse estimate or indication of the bias. However looking at the bias in laboratory intercomparison over years will give a good indication of the performance of the laboratory.

The absolute bias may be dependent upon the concentrations, though the relative bias are considered approximate constant for the concentrations range used in the comparisons. The differences D_i, as defined above are calculated as relative difference, and a median of these relative difference are defined as the QA bias. Median is chosen instead of average to avoid that one outlier get too high influence on the results.

$$\text{QA variability} \quad = \quad \text{RB} = \text{median} \left[\frac{D_i}{T_i} \% \right] \tag{5}$$

If all the data, i.e. 4 of 4 for inorganic- and heavy metal intercomparison, or 8 of 8 for the EC/OC intercomparison, are with the same sign (positive or negative), the RB are denoted with an S to indicate that the analysis systematic under- or overestimate.