Proficiency Tests and Interlaboratory Studies for Good Quality FR Analysis

Jacob de Boer
FR Analysis: Holistic Approach

Sampling → Plan – Objectives – Programme

Storage

Chemical Analysis

Data Analysis

Co-ordination

Assessment

Documentation

TOTAL QUALITY MANAGEMENT

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If we collect bad data:

- E.g. in UK:
  >30,000 analytical labs
  220,000 laboratory analysts
  100,000,000 analytical measurements per year
  3 analytical measurements per sec

**The cost**

Total value of the UK analytical services sector has been estimated to be UK 8.2 billion Euro per year. It has been estimated that 10-20% of results are *not* 'fit-for-purpose', which costs: 

*0.8-1.6 billion Euro per year*
OSPAR

• OSPAR rejects data that doesn’t meet at least minimum QC requirements
• 40 MEuro spent on generating monitoring data
• 50% of data was rejected from database
• 20 MEuros worth of work and it cannot be used

😊
QA/QC - Definitions

- **QA**: All actions carried out to plan the proper performance of the analytical task

- **QC**: All operational techniques and activities that are used to fulfill requirements for quality
QA/QC - Tools

• Workplan
• Guidelines
• Calibration, Blanks
• Reference Materials
• Quality Chart
• Interlaboratory Studies/Proficiency Tests
## Workplan

<table>
<thead>
<tr>
<th>Substance</th>
<th>Matrix</th>
<th>Trend type</th>
<th>Sensitivity</th>
<th>Co-factors</th>
<th>Precautions</th>
<th>Frequency</th>
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<tbody>
<tr>
<td>Metals</td>
<td>Air</td>
<td>Time</td>
<td>%</td>
<td>Fat</td>
<td>Ship</td>
<td>1x/wk</td>
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<tr>
<td>Nutrients</td>
<td>Water</td>
<td>Spatial</td>
<td>mg/kg</td>
<td>Org. C</td>
<td>Containers</td>
<td>1x/month</td>
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<td>Soil</td>
<td>Local</td>
<td>μg/kg</td>
<td>Dry w.</td>
<td>Glassware</td>
<td>1x/year</td>
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<tr>
<td></td>
<td>Sediment</td>
<td>Global</td>
<td>ng/kg</td>
<td>Length</td>
<td>Knives</td>
<td>Continuous</td>
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<tr>
<td></td>
<td>Sludge</td>
<td>Rural</td>
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<td>Weight</td>
<td>Spatula’s</td>
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<td></td>
<td>Dust</td>
<td>Point-source</td>
<td></td>
<td>Age</td>
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<td>Biota</td>
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</table>
Matrix

• Biota: fish, shellfish, other?
• If fish, which type, which length?
• How can we catch them in a representative way?
• Do we need a boat? (costs!)
• Do we pool them or analyse individuals?
• Which part/organ do we analyse?
• How is the transport to the lab?
• Do we need ice/dry ice?
Precautions

- Safety of sampling methods (nets, electricity)
- Do we need a license?
- Are there ethical issues?
- Which materials can cause contamination?
- Pen/paper to record observations?
Target Compounds

• Do we have standards? (order, costs)
• Quality of standards?
• Do we have an instrument to analyse them?
• Can we prepare proper calibration curves?
Required Sensitivity

- What is the expected concentration?
- Is our instruments sensitive enough?
- Do we need a specific detector?
- How much sub-sample do I need?
- How much sample is needed to ensure the minimum size of the sub-sample?
Blanks: DecaBDE in Jelly Fish

GC-ECNI-MS

Comb Jellies
0.014 ng/g ww

Blank (60 fg)
Sediment core
Sampling: Contamination

- Plastic bags
- Ship (oil, dirt, exhaust gasses)
- Knives
- Filters
- Glassware
- Cross contamination
- One species
Effect of Poor Clean up

Insufficient clean up

Suitable clean up

Hexa-mono-ortho-PCBs
Sediments: Sulphur
Co-factors

• Which co-factors are we going to analyse?
• What are the implications for sampling?
• Fat? Which fat? (triglycerides, total fat)?
• TOC – Which method?
• Which method do we need? Is that available?
• Is it validated?
• Is there a reference material?
Sensitivity

1978 – 0.1 mg/kg

1988 – 1 μg/kg

1998 – 1 ng/kg

2008 – 10 pg/kg
Concentration vs. CV

Concentration (ng/g)

CV

Concentration (ng/g) vs. CV

- p,p'-DDE
- g-HCH
- dieldrin
- CB52
- CB153

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Validation

- **Accuracy** = Precision (In-house) and Trueness (External)
- **Precision**: repeatability, reproducibility (IRM - QC Chart)
- **Trueness**: participation in PT scheme and use of CRM
- **Linearity**: calibration curves (multi-level if not linear)
- **Detection Capability**: LOD and LOQ: signal-to-noise level, blanks
- **Robustness/Ruggedness**: sensitivity for interference, dependency of matrix, influence of technician, etc.
Accuracy

- Poor trueness
- Poor precision

- Poor trueness
- Good precision

- Good trueness
- Poor precision

- Good trueness
- Good precision
Precision

• **Repeatability**
  - 5 replicates of e.g. LRM analysed in one series at one day by one technician at one instrument

• **Reproducibility**
  - 5 replicates of e.g. LRM analysed in different series at different days by different technicians at different instruments
Ruggedness

The ability of a method to be relatively insensitive to minor changes in the procedure, to the quality of reagents or to the environment
| Waarneming | 221 | 222 | 223 | 224 | 225 | 226 | 227 | 228 | 229 | 230 | 231 | 232 | 233 | 234 | 235 | 236 | 237 | 238 | 239 | 240 | 241 | 242 | 243 | 244 | 245 | 246 | 247 | 248 | 249 | 250 |
|-----------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Gehalte in µg/kg |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| opmerking |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| Affleurings X |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |

**Gegevens over voorgaande perioden**

| Gem +3S  | → 552.8 |
| Gem +2S  | → 502.5 |
| Gem   | → 465.9 |
| Gem +2S | → 394.1 |
| Gem -3S | → 359.1 |
| N   | → 148 |
| N zeven | → 150 |
| Nwaarn.  | → 2 |
| Standev.| → 22.3 |

**Gegevens over deze periode**

| Gem +3S  | → 534.3 |
| Gem +2S  | → 500.9 |
| Gem   | → 461.1 |
| Gem +2S | → 412.3 |
| Gem -3S | → 387.9 |
| N   | → 30 |
| Standev.| → 24.4 |

**Gegevens over alle waarnemingen**

| Gem +3S  | → 545.3 |
| Gem +2S  | → 513.7 |
| Gem   | → 450.4 |
| Gem +2S | → 387.5 |
| Gem -3S | → 355.5 |
| N   | → 243 |
| N zeven | → 250 |
| Nwaarn.  | → 7 |
| Standev.| → 31.6 |

**Na 30 waarnemingen:**

\[
\text{Na 30 waarnemingen:}
\]

\[
\frac{\text{Na 30 waarnemingen}}{\text{Na 30 waarnemingen}}: 1.32
\]

**Kwantiel waarde:* 1.48**

**Kwantiel waarde:* 1.58**
External Quality Control

• Interlaboratory Studies/Proficiency Tests
• Certified Reference Materials (CRMs)
Interlaboratory Studies

• One-off Studies
• Stepwise-designed studies (Learning exercises)
• Proficiency tests

Advantage: blind tests

We need interlab studies for

▪ Comparability of data
▪ For trueness
▪ For accreditation purposes
Stepwise Designed Interlaboratory Studies:

- **Real samples**
- **Uncleaned Extracts**
- **Clean Extracts**
- **Solutions**

Advice in every round
Proficiency Tests

- Routine schemes
- Regular distribution of test materials (e.g. 1 or 2x per year)
- Direct report to participants
- Use of Z-scores
- Useful and mandatory for accreditation

Also: blind tests
Requirements:
How Good should it be?

Assume we need to detect a 50% change in contaminant level,

* e.g. a decrease from 8 to 4:

Max. allowed CV should be ca. 25%, because in that case 8 may
be 6 or 10 or in between, and 4 maybe 3 or 5 or in between:

\[
6 < 8 < 10, \text{ and: } 3 < 4 < 5
\]
Z-scores

\[ z = \frac{(m - \mu)}{sd} \]

Example: \( \mu = 20 \), target st. dev. = 25% = 5,
- When result is 30 \( \Rightarrow \) Z-score = \( 30 - 20 / 5 = 2 \)
- When result is 40 \( \Rightarrow \) Z-score = \( 40 - 20 / 5 = 4 \)
Z-scores

\[ |Z| < 2 \text{ Satisfactory performance} \]
\[ 2 < |Z| < 3 \text{ Questionable performance} \]
\[ |Z| > 3 \text{ Unsatisfactory performance} \]
\[ |Z| > 6 \text{ frequently points to gross errors (mistakes with units during reporting, calculation or dilution errors, and so on).} \]
The assigned value
Probability Density Function

$(\sum \text{OMFs})^2 = \text{Population Density Functions (PDFs) for BWE}$

- **QOR076MS CB153**
- **BLACK dots for histogram of All Data**
- **BLUE area** for Mode 1 PDF
- **GREEN area** for All Data

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- **IVM Institute for Environmental Studies**
$(\sum \text{OMFs})^2 = \text{Population Density Functions (PDFs) for BWE}$

QOR053BT  CB156
BLACK dots for histogram of All Data
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GREEN area for All Data
Different statistics

• PT providers use different statistics, e.g. with different treatment of outliers
• Outlier tests, e.g. : Grubb’s test
• Robust statistics: downweighting outliers
• Multivariate statistics
• Cofino statistics: probability density function
'Kilt’-Plot

Kilt Plot (Overlap Matrix) – BWE QOR076MS CB153

Kilt Plot (Overlap Matrix) – BWE QOR053BT CB156
QUASIMEME: ‘Holistic Approach’

- Proficiency Tests
  - POPs, PAHs, Trace metals, Nutrients, Shellfish Toxins
- Learning Exercises
  - ‘New’ Contaminants
- Training Workshops
- Internet Exchange of Technical Questions
- Monitoring Long Term Performance Labs
### Results of Interlaboratory Studies for PCBs & OCPs

<table>
<thead>
<tr>
<th>Year</th>
<th>No. Labs</th>
<th>Matrix</th>
<th>R.S.D. PCB%</th>
<th>R.S.D. OCP%</th>
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<tbody>
<tr>
<td>2009-10</td>
<td>37</td>
<td>Sed</td>
<td>42</td>
<td>117</td>
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<tr>
<td>2006-10</td>
<td>7</td>
<td>Sed</td>
<td>150</td>
<td>130</td>
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<td>2002</td>
<td>78</td>
<td>Sed</td>
<td>1-160</td>
<td>45-140</td>
</tr>
<tr>
<td>1998</td>
<td>48</td>
<td>Sed</td>
<td>19-180</td>
<td>47-150</td>
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<tr>
<td>1997</td>
<td>40</td>
<td>Sed</td>
<td>25</td>
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<td>2000</td>
<td>55</td>
<td>Herring</td>
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<td>70</td>
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<tr>
<td>1993</td>
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<td>90</td>
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<tr>
<td>1988</td>
<td>-</td>
<td>Fish</td>
<td>41</td>
<td>39</td>
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<tr>
<td>1997</td>
<td>3</td>
<td>Tuna</td>
<td>41</td>
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<td>45-140</td>
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<td>39</td>
</tr>
</tbody>
</table>
Trends in Performance of Laboratories

- CBs % Labs with > 90% data | Z | <2
- CBs % Labs with > 75% data | Z | <2
- OCPs % Labs with > 90% data | Z | <2
- OCPs % Labs with > 75% data | Z | <2

Year

% Labs with satisfactory data
- 0
- 10
- 20
- 30
- 40
- 50
- 60

% Labs with > 90% data
- 0
- 10
- 20
- 30
- 40
- 50
- 60

% Labs with > 75% data
- 0
- 10
- 20
- 30
- 40
- 50
- 60

Legend:
- CBs % Labs with > 90% data | Z | <2
- CBs % Labs with > 75% data | Z | <2
- OCPs % Labs with > 90% data | Z | <2
- OCPs % Labs with > 75% data | Z | <2
- BDE99 in standard solution
- BDE 47 in fish
- BDE47 in sediment
- BDE47 in sediment (II)
Table 1 Summary Statistics for QUASIMEME Participants

<table>
<thead>
<tr>
<th>Matrix/terminand</th>
<th>Assigned</th>
<th>Units</th>
<th>Total</th>
<th>NObs</th>
<th>NObs</th>
<th>Median</th>
<th>Robust</th>
<th>Between</th>
<th>Model</th>
<th>Model s.d.</th>
<th>Model CV%</th>
<th>% data Model</th>
</tr>
</thead>
<tbody>
<tr>
<td>3C005MS</td>
<td>0.513</td>
<td>ug/kg</td>
<td>22.25</td>
<td>6</td>
<td>6</td>
<td>0.51</td>
<td>0.52</td>
<td>26.14</td>
<td>0.51</td>
<td>0.02</td>
<td>3.35</td>
<td>53.18</td>
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<tr>
<td>3DE028</td>
<td>7.828</td>
<td>ug/kg</td>
<td>13.14</td>
<td>1</td>
<td>1</td>
<td>7.76</td>
<td>7.76</td>
<td>23.62</td>
<td>7.83</td>
<td>1.38</td>
<td>17.69</td>
<td>61.73</td>
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<td>3DE047</td>
<td>11.248</td>
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<td>12.94</td>
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<td>8</td>
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<td>11.11</td>
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<td>53.66</td>
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<td>3DE100</td>
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<td>17.00</td>
<td>8</td>
<td>8</td>
<td>1.15</td>
<td>1.22</td>
<td>39.05</td>
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<td>1.01</td>
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<th>Model CV%</th>
<th>% data Model</th>
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<tr>
<td>HBCD</td>
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<td>ug/kg</td>
<td>12.49</td>
<td>2</td>
<td>2</td>
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<td>6.80</td>
<td>83.79</td>
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<td>0.00</td>
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<tr>
<td>TBBP-A</td>
<td>12.49</td>
<td>ug/kg</td>
<td>12.49</td>
<td>2</td>
<td>2</td>
<td>6.80</td>
<td>6.80</td>
<td>83.79</td>
<td>6.80</td>
<td>0.00</td>
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<tr>
<td>Ethyl-TBBP-A</td>
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<td>ug/kg</td>
<td>12.49</td>
<td>2</td>
<td>2</td>
<td>6.80</td>
<td>6.80</td>
<td>83.79</td>
<td>6.80</td>
<td>0.00</td>
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</thead>
<tbody>
<tr>
<td>3C006MS</td>
<td>0.024</td>
<td>ug/kg</td>
<td>50.00</td>
<td>5</td>
<td>5</td>
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