QMEQAS
The Quebec Multielement External Quality Assessment Scheme

“Experiences and other issues”

Alain LeBlanc
Centre de toxicologie - INSPQ

COPHES Workshop, Nov 30th, 2011 - Brussels, Belgium
Overview

Our organization in pictures

QMEQAS

• Participants
• Scheme operation
• Statistical treatment
• Performance
• Reference materials

Issues and results comparability

➢ A look at phthalate metabolite standards
A few words on the National Public Health Institute of Quebec (INSPQ)

The INSPQ is a government body created in 1998 to improve the coordination, development and use of expertise in public health.

Its creation involved integrating the province's principal public health laboratories and centres of expertise and transferring and assigning staff from a number of regional public health departments and from the Ministry of Health.
Mission of the INSPQ

To support the Ministry of Health and the regional boards in executing their public health mission.
To contribute to the development and application of expertise in the area of public health.
To manage the laboratories and centres in Québec which offer expertise in public health:

- Québec Public Health Laboratory (infectious diseases and pathogens)
- Centre d'expertise en dépistage (mobile screening units for radiology and audiology)
- Centre de toxicologie du Québec (human toxicology)
Le Centre de Toxicologie du Québec

Commissioned by the Quebec government for the detection of intoxications.
  • Drugs / drugs of abuse
  • Monitoring of workers potentially exposed to heavy metals.

Environmental components were rapidly added with the monitoring of exposed populations to different contaminants: Pesticides, herbicides, POP's, etc.

The expertise acquired over time quickly designated the Centre de Toxicologie as a leader in the analysis of environmental contaminants.
OUR ORGANIZATION IN PICTURES
Institut National de Santé Publique du Québec
75 staff members
1200 m² floor surface
ISO 17025 / 17043

Analytical toxicology
Clinical toxicology
Biomedical technology
ICP-MS Instrumentation
GC-MS and GC-MS-MS technology
Automated solid phase extraction modules
JANUS robotic instrument
Phthalate metabolites
Perfluorinated compounds
OH-PAH metabolites
PCBs
PBDEs
Metals
Bisphenol-A
Pesticides
Drugs of abuse
QMEQAS
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External Quality Assessment Schemes (EQAS)

Since 1979

More than 30 countries

250 laboratories
Some historical events

1979 : First EQAS (PCI) for metals in biological samples
1996 : QMEQAS, formerly known as the *ICP-MS Comparison program*, is born
1997 : First scientific symposium among participants
1999 : Second scientific symposium
2000 : ISO 17025 accreditation
2001 : The AMAP EQAS is introduced: PCBs and organochlorinated pesticides in plasma
2006 : CAN-P 43 accreditation (ISO guide 43 and ILAC G-13) as a proficiency testing scheme provider (now ISO 17043)
QMEQAS PARTICIPANTS
STATISTICS
(N = 66)
Organization

Private: 47%
Government: 38%
University: 15%
Profile

Hospital
23%

Specialised Lab
64%

Other
13%
Accreditation

ISO 17025: 26%
Other: 15%
None: 54%
ISO 15189: 5%
ICP-MS instrument

- Low Res: 28%
- DRC: 43%
- CC: 17%
- CRI: 6%
- High Res: 4%
- (ICP-OES): 2%
- Low Res: 28%
Instrument models

- Varian 820-MS: 3%
- Varian Vista Pro Axial ICP-OES: 3%
- Agilent 7500: 10%
- Finnegan Mat Element: 5%
- Thermo Electron: 5%
- VG: 5%
- PE DRC: 39%
- PE Elan 6000: 22%
- PE Elan 9000: 8%
Other types of analyses

Clinical

- Drugs of abuse
- Therap. Drugs
- Alcohol

Environmental

- Pesticides
- PCBs/OCs
- Phthalate metabolites
Geographical distribution of participants
Scheme evolution

- Participants
- Analytes
- Atomic Absorption
SCHEME OPERATION
Scheme operation

- 2012 registration fee: $450 CND (325 EUR)
- All PT materials from human samples
- Assured confidentiality of participants (Lab code)
- 3 annual runs (January, May, September)
- 3 matrices per run (blood, urine and hair)
- 26 elements of potential biological interest
  Ag, Al, As, Ba, Be, Bi, Cd, Co, Cr, Cu, Hg, I, Mn, Mo, Ni, Pb, Pt, Sb, Se, Sn, Te, Th, Tl, U, V, Zn
Evolution of the STATISTICAL TREATMENT of data
Prior to 2010

Calculated parameters

- N
- Average
- Median (1)
- Median (2) *after removing outliers*
- Standard deviation
- % variation coefficient
Removing outliers

- **MAD = Median Absolute Deviation**
  \[
  \text{MAD} = \text{median } |(x_i - \text{initial median})| \\
  \text{for } i = 1 \text{ to } n \text{ where } n = \text{number of participants.}
  \]

- Hampel’s test: Results for which
  \[
  |x - \text{initial median}| > 3 \times 1.4826 \text{ MAD}
  \]
  are eliminated; a new median is calculated.
Performance

- \textit{assigned value} = median (2)

But \textit{assigned value} = consensus median obtained through the PCI program if available. (more representative of the “true value”)

- Participants rated using z-scores

\[
z = \frac{x - \text{assigned value}}{\text{assigned deviation}}
\]
Assigning fixed performance criteria

<table>
<thead>
<tr>
<th>Concentration range (µg/L)</th>
<th>Maximum accepted error</th>
<th>Assigned deviation</th>
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<tbody>
<tr>
<td>&lt; 0.5</td>
<td>100 %</td>
<td>33.3 %</td>
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<tr>
<td>0.5 - 2</td>
<td>50 %</td>
<td>16.7 %</td>
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<tr>
<td>2 - 5</td>
<td>30 %</td>
<td>10 %</td>
</tr>
<tr>
<td>&gt; 5</td>
<td>20 %</td>
<td>6.7 %</td>
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</tbody>
</table>
**z-score criteria**

<table>
<thead>
<tr>
<th>z-score</th>
<th>Performance</th>
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</thead>
<tbody>
<tr>
<td>≤ 2</td>
<td>Satisfactory</td>
</tr>
<tr>
<td>&gt; 2 and &lt; 3</td>
<td>Questionable</td>
</tr>
<tr>
<td>≥ 3</td>
<td>Unsatisfactory</td>
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</table>
### QMEQAS09B-02 Pb

<table>
<thead>
<tr>
<th>Participant</th>
<th>Résultat</th>
<th>cote-z</th>
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<tr>
<td>L1</td>
<td>236</td>
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<td>L2</td>
<td>242</td>
<td>0.1</td>
</tr>
<tr>
<td>L3</td>
<td>247</td>
<td>0.5</td>
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<tr>
<td>L7</td>
<td>252</td>
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<td>L9</td>
<td>223</td>
<td>-1.1</td>
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<td>L11</td>
<td>251</td>
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<td>L12</td>
<td>240</td>
<td>0.0</td>
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<td>L18</td>
<td>233</td>
<td>-0.4</td>
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<td>L21</td>
<td>225</td>
<td>-0.9</td>
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<td>L22</td>
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<td>L26</td>
<td>234</td>
<td>-0.4</td>
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<tr>
<td>L29</td>
<td>248</td>
<td>0.5</td>
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<tr>
<td>L30</td>
<td><strong>22</strong></td>
<td>-13.6</td>
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<tr>
<td>L32</td>
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<td>240</td>
<td>0.0</td>
</tr>
<tr>
<td>L37</td>
<td>240</td>
<td>0.0</td>
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<tr>
<td>L38</td>
<td>236</td>
<td>-0.2</td>
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<tr>
<td>L39</td>
<td>257</td>
<td>1.1</td>
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<td>L42</td>
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<td>-0.2</td>
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<tr>
<td>L53</td>
<td>247</td>
<td>0.5</td>
</tr>
<tr>
<td>L56</td>
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<td>1.9</td>
</tr>
<tr>
<td>L57</td>
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<td>L58</td>
<td>242</td>
<td>0.1</td>
</tr>
<tr>
<td>L60</td>
<td>211</td>
<td>-1.8</td>
</tr>
<tr>
<td>L62</td>
<td>235</td>
<td>-0.3</td>
</tr>
<tr>
<td>L65</td>
<td>250</td>
<td>0.6</td>
</tr>
<tr>
<td>L66</td>
<td>232</td>
<td>-0.5</td>
</tr>
</tbody>
</table>

**Moyenne / Mean:** 241  
**Médiane / Median:** 240  
**Écart type / Std. Dev.:** 13  
**C.V.:** 5%  
**N:** 28

(avec aberrants / with outliers)

<table>
<thead>
<tr>
<th>Dév. désignée absolue</th>
<th>16</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abs. assigned deviation</td>
<td></td>
</tr>
</tbody>
</table>

PCI : s.o. / NA  
Ajout / Spiked : 225

<table>
<thead>
<tr>
<th>Valeur désignée</th>
<th>240</th>
</tr>
</thead>
<tbody>
<tr>
<td>Assigned value</td>
<td></td>
</tr>
</tbody>
</table>
2010 onwards

• Assigned Value (AV) : Algorithme A (ISO 13528)
• Uncertainty
• No outliers removed except if error can be explained
• Acceptable range (σ_{PT})
• Z’ scores (accounts for the uncertainty around the AV)
• Statistics for all methods and per type of method
• Kolmogorov-Smirnov normality test
Assigned values by consensus

Serum aluminum (nmol/L)
Proficiency standard deviation ($\sigma_{PT}$)

Urine Lead

$y = 0.0794x + 0.0026$
BUT WHAT ABOUT PERFORMANCE?
Hair performance
z-score ≤ 2

- As
- Cr
- Mo
- Ni
- Pb
- Se
- Hg
Hair metals z-scores Run 2009-1

- ≤ 2
- > 2 and < 3
- ≥ 3 + outliers

Cd, Mo, Pb, As, Ni, Se, Hg, Cr
Urine Cadmium: Median $|Z|$.

The graph shows the relationship between Median Z-Score and Sequential Sample Number. The regression line is given by the equation:

$$y = -0.0018x + 0.6141$$
REFERENCE MATERIALS

ISO/CEI 17043
Preparation of proficiency testing materials

Human biological matrices
Not freeze dried
Stable
Homogenous
Steps in the making of PTMs

- Design
- Getting the raw material
- Adding the analytes
- Testing for infectious diseases (Blood)
- Aliquoting
- Determination of homogeneity and stability (ISO 13528)
- Preservation
- Distribution within scheme
Validation - Stability

Adding a new analyte

→ Stability study
  (ISO 13528 :2005)

- Same analytical method than for testing homogeneity
- Same PT materials than for testing homogeneity
Validation - Stability

Validation of the stability for the duration of the PT exercise:

- 9 materials (3 at each temperature)
- -20°C, 4°C et room temperature
- Duration: 8 weeks
- Reference temperature: -20°C
- $\leq 0,3 \sigma_{pt}$ between averages at each T
Validation - Homogeneity

- For each PT
- For each cycle
- 8 or 9 samples (3 measures each)

\[
\text{Heterogeneity} \leq 0.3 \sigma_{PT}
\]

**Criterion:**
Past participants’ performance
Validation - Homogeneity

QMEQAS10B09

Relative concentration vs. Tube #

Cu
Eu
Reference material virtual store

Welcome to our virtual store where you will find reference material on toxicology. This material originates from our External Quality Assessment Schemes.

To order, you must first register.

If you are already registered, please enter your username and password in the appropriate boxes (top right of screen).

To consult the list of available reference material or to order, please click on "Reference Material" in the top menu.

"My basket" and "My profile" are available only to those who have already registered.

If you have forgotten your password, click here

This page was last updated on February 23, 2007
### Available analytes

<table>
<thead>
<tr>
<th>Analyte</th>
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<tbody>
<tr>
<td>B-2-microglobulin</td>
</tr>
<tr>
<td>Blood Cadmium</td>
</tr>
<tr>
<td>Blood Lead</td>
</tr>
<tr>
<td>Blood Mercury</td>
</tr>
<tr>
<td>Non-dietary Arsenic</td>
</tr>
<tr>
<td>PMQAS blood</td>
</tr>
<tr>
<td>PMQAS Urine</td>
</tr>
<tr>
<td>QMEQAS Blood</td>
</tr>
<tr>
<td>QMEQAS Hair</td>
</tr>
<tr>
<td>QMEQAS Serum</td>
</tr>
<tr>
<td>QMEQAS Urine</td>
</tr>
<tr>
<td>Serum Aluminium</td>
</tr>
<tr>
<td>Serum Copper</td>
</tr>
<tr>
<td>Serum Manganese</td>
</tr>
<tr>
<td>Serum Selenium</td>
</tr>
<tr>
<td>Serum Zinc</td>
</tr>
<tr>
<td>Urine Arsenic</td>
</tr>
<tr>
<td>Urine Cadmium</td>
</tr>
<tr>
<td>Urine Chromium</td>
</tr>
<tr>
<td>Urine Copper</td>
</tr>
<tr>
<td>Urine Fluoride</td>
</tr>
<tr>
<td>Urine Lead</td>
</tr>
<tr>
<td>Urine Mercury</td>
</tr>
<tr>
<td>Urine Selenium</td>
</tr>
<tr>
<td>Urine Zinc</td>
</tr>
</tbody>
</table>

### Other available products

<table>
<thead>
<tr>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>BPC/OC in serum</td>
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</table>
## QMEQAS Urine

<table>
<thead>
<tr>
<th>Control number</th>
<th>Stock</th>
<th>Price (us $)</th>
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<tr>
<td>QMEQAS05U02</td>
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<td>35</td>
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<td>QMEQAS05U05</td>
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<td>35</td>
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<td>QMEQAS05U08</td>
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<td>35</td>
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<tr>
<td>QMEQAS06U01</td>
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<td>35</td>
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<tr>
<td>QMEQAS06U04</td>
<td>47</td>
<td>35</td>
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<tr>
<td>QMEQAS06U07</td>
<td>82</td>
<td>35</td>
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<td>QMEQAS07U02</td>
<td>41</td>
<td>35</td>
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<tr>
<td>QMEQAS07U05</td>
<td>49</td>
<td>35</td>
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<tr>
<td>QMEQAS07U08</td>
<td>41</td>
<td>35</td>
</tr>
<tr>
<td>QMEQAS08U01</td>
<td>117</td>
<td>35</td>
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<tr>
<td>QMEQAS08U04</td>
<td>58</td>
<td>35</td>
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<tr>
<td>QMEQAS08U07</td>
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<td>35</td>
</tr>
<tr>
<td>QMEQAS09U03</td>
<td>60</td>
<td>35</td>
</tr>
</tbody>
</table>

Consult the [evaluation report](#)
Reference materials virtual store

Materials remaining from previous PT cycles are made available to participants and other interested laboratories.

www.inspq.qc.ca/ctq/sales
Issues and results comparability

Case #1
QMEQAS versus PMQAS
Observed Performance for PMQAS and QMEQAS
Urine cadmium "Z-scores"

Criterion = 10%
<table>
<thead>
<tr>
<th>Instrument Models</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Varian 820-MS</td>
<td>3%</td>
</tr>
<tr>
<td>Finnegan Mat Element</td>
<td>5%</td>
</tr>
<tr>
<td>Thermo Electron</td>
<td>5%</td>
</tr>
<tr>
<td>VG</td>
<td>5%</td>
</tr>
<tr>
<td>PE Elan 6000</td>
<td>22%</td>
</tr>
<tr>
<td>PE Elan 9000</td>
<td>8%</td>
</tr>
<tr>
<td>Varian Vista Pro Axial</td>
<td>3%</td>
</tr>
<tr>
<td>Agilent 7500</td>
<td>10%</td>
</tr>
<tr>
<td>PE DRC</td>
<td>39%</td>
</tr>
</tbody>
</table>
Observed Performance for PMQAS and QMEQAS

Urine cadmium "Z-scores"

Criterion = 10%
Issues and results comparability

Case #2

Accuracy of analytical standards in the case of emerging contaminants: Phthalate metabolites
The CTQ experience

Method developed in 2006 to take part in the biomonitoring initiative of the Canadian Health Measures Survey: **CHMS-I** (2500 samples)

Further studies:

- **CHMS-II**  Canadian Health Measures Survey (2740 samples)
- **MIREC**  Maternal-Infant Research on Environmental Chemicals (1500 samples)
- **P4**  Plastics and Personal care Products in Pregnancy (1600 samples)
- **FNBI**  First Nations Biomonitoring Initiative (800 samples)

Method:

- 13 metabolites (mono esters)
- Automated SPE extraction on 96 well plate, anion exchange
- **UPLC-MS-MS**
- Under ISO 17025 guidelines
What’s the concern?

Certain results from our laboratory fall outside the performance criteria of the G-EQAS program

- German External Quality Assessement Scheme
- Details:
  - Twice a year interlaboratory comparison
  - 5 to 9 participants
  - 3 to 5 analytes
Preliminary investigation

1) A closer look at our internal QC chart
2) Return on the raw data:
   - Calibration curves, slopes, integration, data processing, contamination, etc...
3) Tracability of the standards and solutions
4) Analyst?
5) Repeated analyses (2x, 3x, 4x …)
6) Purchase of a similar lot of standards (same results…)
7) Doubts set in…
   - How can the results be biased considering that the internal quality control indicates that the method is under control? The whole method would be biased? … the analytical standards?
A second investigation

1) Comparing two different CERTIFIED lots of standards from Cambridge Isotope Laboratories (CIL) in our possession
   **Surprise #1 !**

2) Meeting with CIL
   - No lot-to-lot comparison…
   - No problem…

3) Search to identify reliable standards (accurate)
   - important limitation: only one commercial supplier worldwide…
   - Custom synthesis of all the metabolites at CanSyn (neat)

4) Comparing the two sets from CIL with the one from CanSyn…
   **Surprise #2 !**
Pushing a bit further...

1) Searching for other potential commercial suppliers for a maximum of analytes:
   - Insufficient number

2) Order by custom synthesis in another supplier:
   - Toronto Research Chemicals TRC (neat)

3) Order of a third series of standards from CIL… neat form.

4) Comparing all lots from all suppliers for all the analytes…
   - 95 standards:
     - 13 metabolites
     - 12 sets of standards
     - 7 suppliers
     - 2 forms (certified solutions and neat)
     - $$$ (50-60K)

5) Surprise #3!
Standards’ comparison

Comparison done with regard to CIL neat (triplicate)

<table>
<thead>
<tr>
<th>Supplier</th>
<th>MMP</th>
<th>MEP</th>
<th>MiBP</th>
<th>MnBP</th>
<th>MCHP</th>
<th>MBzP</th>
<th>MEHP</th>
<th>MEHHP</th>
<th>MEOHP</th>
<th>MECPP</th>
<th>MOP</th>
<th>MCP</th>
<th>MNP</th>
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<tbody>
<tr>
<td>CIL-2006</td>
<td><strong>-25%</strong></td>
<td><strong>-2%</strong></td>
<td>-</td>
<td><strong>-47%</strong></td>
<td>-1%</td>
<td><strong>-63%</strong></td>
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<td><strong>-7%</strong></td>
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<td><strong>12%</strong></td>
<td><strong>-22%</strong></td>
<td><strong>-39%</strong></td>
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<td>CIL-2009</td>
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<td>4%</td>
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<td>-70%</td>
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<td>CIL-2010</td>
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<tr>
<td>Accustandard</td>
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<td>-31%</td>
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<td>-4%</td>
<td>-27%</td>
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<td>Chiron</td>
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Re-analysis of the G-EQAS materials

The case of MnBP

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Consequences

- Innaccurate results
- Comparability of results…
  - Intra- and interlaboratory, if using different lots of standards
  - Biomonitoring studies
- Low reliability…
  - Interpretation of results
  - Past data ?
- Questioning credibility…
  - of laboratories
  - of standards’ suppliers
Proposed solutions

**Suppliers:**
- Investigate and resolve the innacurary issue of the *certified* solutions.
- Compare the accuracy of standards when switching from one lot to another.
- Provide the comparison data on the certificates of analysis.

**Laboratories:**
- For the time being, use ONLY standards in their « neat » form.
- Verify accuracy of standards with a second reliable source.
Conclusion

- Certified standards are not necessarily accurate, even more so for emerging compounds for which there is a very limited number of suppliers.
- Data generated within External Quality Assessment Schemes can be biased due to the inaccuracy of standards used.
- It is important to stay alert when interpreting biomonitoring data.
Acknowledgements

Isabelle Côté, chemist……….PCI coordinator

Eric Langlois, chemist……….Method development phthalate metabolites
THANK YOU!

Château Frontenac, Quebec City