# *Experiences from PT-WFD proficiency tests on polybrominated diphenylethers and alkylphenols*

**Ulrich Borchers***, **Friedrich Werres (IWW Water Centre, DE),**
**Michael Koch, Frank Baumeister (AQS-BW, DE)**

Eurachem
A focus for analytical chemistry in Europe

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IWW
IWW Rheinisch-Westfälisches Institut für Wasser
Beratungs- und Entwicklungsgesellschaft mbH

iswa
AQS Baden-Württemberg

# Topics

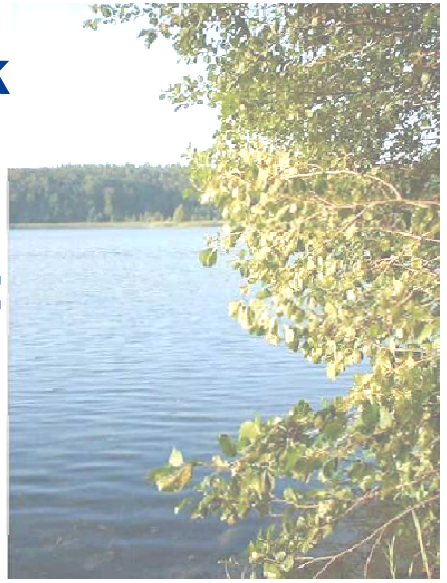
- **Scope of the PT-WFD Network**
  - Objectives and Parameter Spectrum
  - Sample Matrix and Concentrations
  - Performance Requirements
- **PT on Polybrominated Diphenylethers**
  - Specific problems
- **PT on Alkylphenols (and Bisphenol-A)**
  - Specific problems
- **Conclusions**

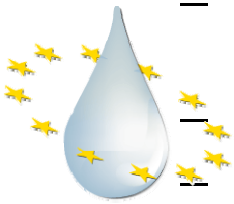
# Objectives of the PT-WFD network

- **Specially designed for EU Water Framework Directive Purposes (WFD)**

- **Important statement of the EU Commission:**
  - The implementation of the WFD requires the design of monitoring programmes ensuring
    - the reliability and
    - comparability of monitoring data
      - Including traceability aspects

- **The QA/QC Commission Directive 2009/90/EC requires that**
  - monitoring labs demonstrate their competence by participation in suitable PT programmes
  - covering all relevant analytes
  - in relevant matrices (surface waters)
  - at concentrations representative for WFD



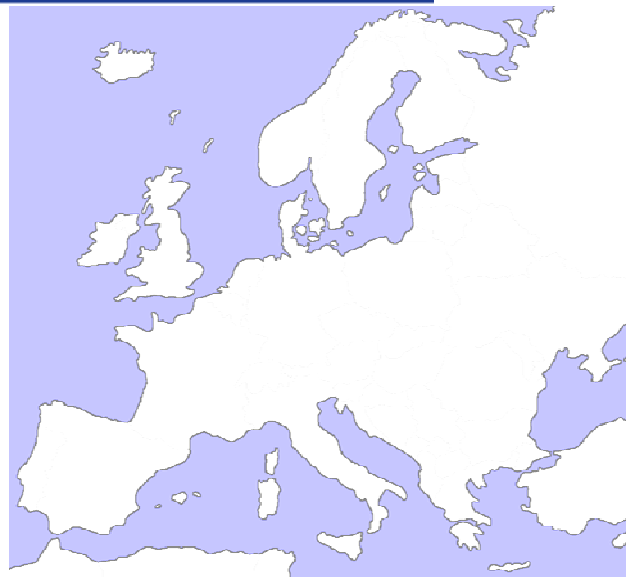


# QA/QC Commission Directive (2009/90/EC)

- **Standardised and other validated methods**
- **Requirements on analytical methods**
  - Validation according to EN ISO 17025
  - **Limit of Quantification (LOQ)**
    - **≤ 30 % of the relevant EQS**
  - **Relative Target Uncertainty at EQS level**
    - **≤ 50 %**
  - (EQS = Environmental Quality Standards)
- **If there is no EQS or no method that meets the performance criteria**
  - best available techniques
  - not entailing excessive costs

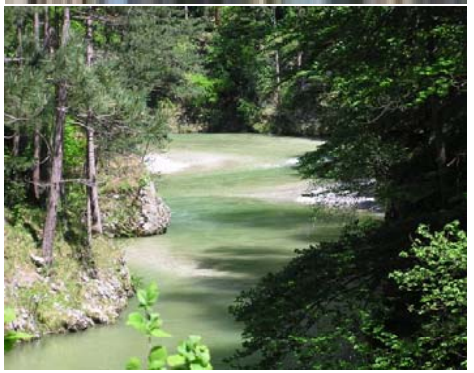
# Benefits of the harmonisation of PTs

- **Comparability of monitoring data obtained throughout Europe**
- **Access to relevant PTs also by labs in smaller countries**
  - **Some trace analytes are analysed just by very few labs in each country**
- **Decreasing costs of test samples**
- **Know how transfer**
- **Regular survey of gaps and initiation of new developments**



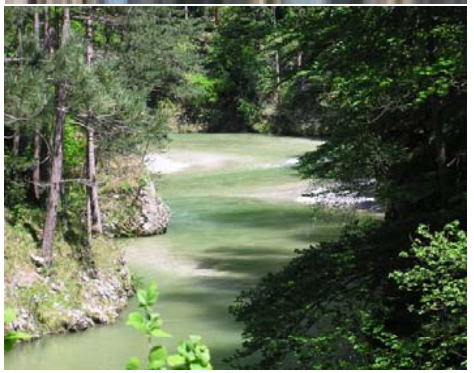
# Essentials and unique features…..

- **Analysis of whole water samples**
  - Containing particles (SPM) up to 500 mg/l
  - Analytes may be bound to the solid phase
    - non-polar (sorptive) substances
- **Real or spiked real samples**
- **Very low concentrations**
  - due to challenging EQS values
- **Priority Substances according to WFD**
  - Complex analytical requirements
  - Some standardised methods not adapted to the requirements (fitness-for-purpose?)
  - Relation between limits and methods for sum/consensus parameters



# …. are causing specific problems in PTs

- **Preparation of homogeneous samples with SPM**
- **Insufficient extraction of samples**
  - **Due to poor method description**
  - **Due to poor experience of labs**
- **Lack of method sensitivity**
- **Divergencies between Limit (EQS) and analyte definition**



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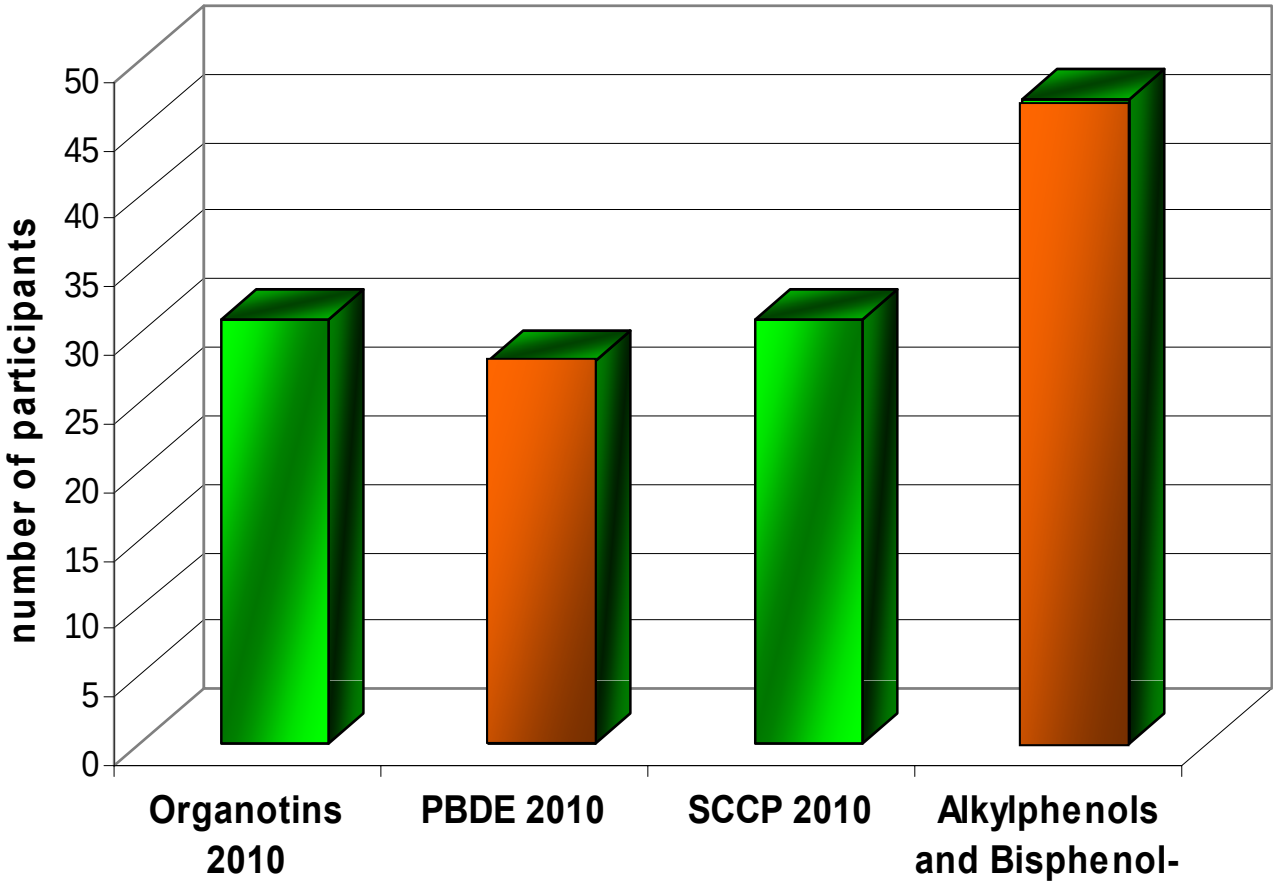
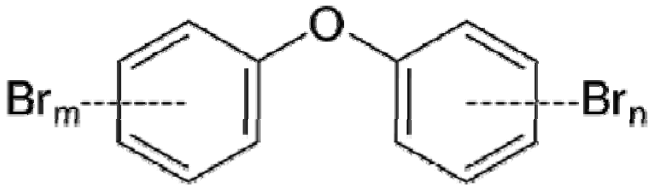
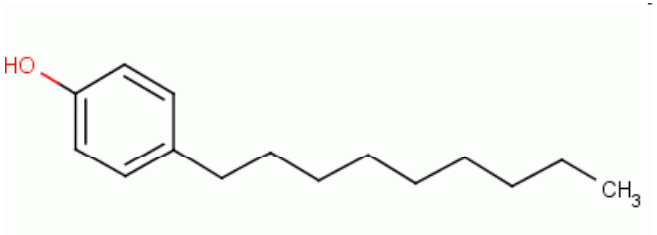
# Examples from PT rounds 2010

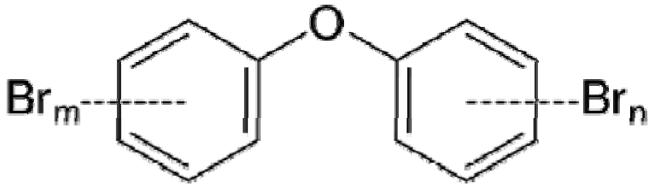


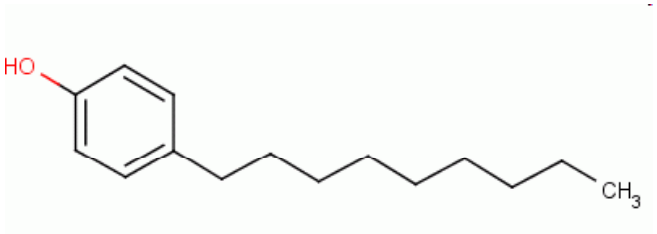



# Examples from PT rounds 2010

| | AA-EQS [ng/l] | PT concentration range [ng/l] |
|---|---|---|
| Priority Substances | | |
| **2,4,4-Tribromodiphenylether (BDE 28)** | **0.5** | **0.8-9** |
| **2,2,4,4-Tetrabromodiphenylether (BDE 47)** | **0.5** | **1-11** |
| **2,2,4,4,5-Pentabromodiphenylether (BDE 99)** | **0.5** | **1-12** |
| **2,2,4,4,6-Pentabromodiphenylether (BDE 100)** | **0.5** | **1-10** |
| **2,2,4,4,5,5-Hexabromodiphenylether (BDE 153)** | **0.5** | **1-11** |
| **2,2,4,4,5,6-Hexabromodiphenylether (BDE 154)** | **0.5** | **1-10** |



# Matrix and other relevant information

- **Matrix**
  - Filtered surface water
    - 5 µm and, 1 µm, UV radiation
    - Particles smaller than 1 µm not removed
  - 3 x 2 different surface water samples at three concentration levels in 1 L ground glass bottles
- **Sample preservation by cooling**
- **Methods**
  - No standardised method for water
  - Liquid-liquid extraction (LLE)
  - HRGC-MS and HRGC-MS/MS

# Evaluation according to Network agreement

- **Assigned value X:**
  - **Consensus Mean or**
  - **Reference value (spike + matrix content)**

- **Standard deviation for proficiency assessment (SDPA):**
  - **0,25 x X**
  - **This means 25 % RSD**

- **Assessment:**

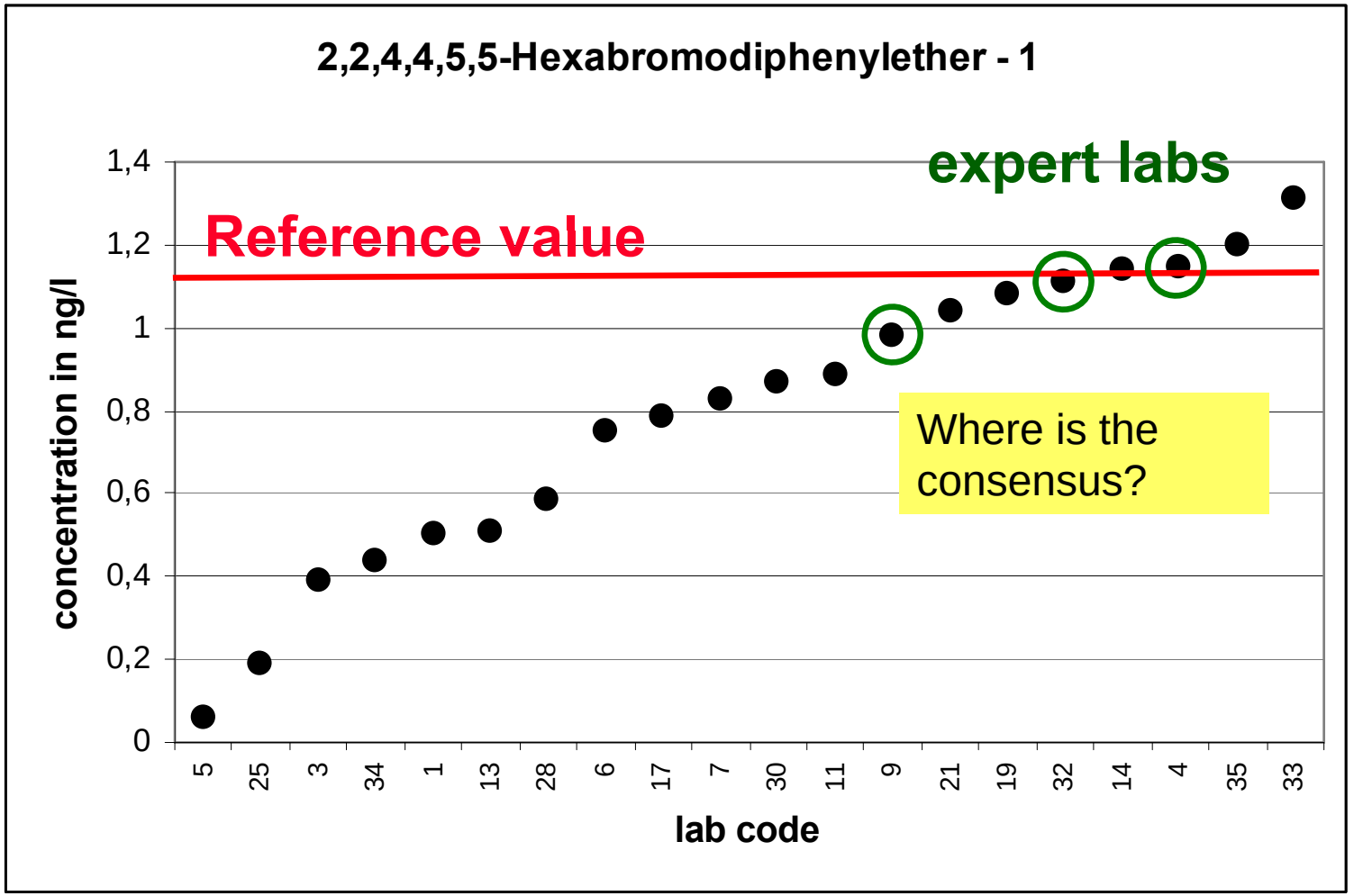
$$|\text{z-score}| \leq 2.0 \quad \text{Satisfactory result}$$

$$2.0 < |\text{z-score}| < 3.0 \quad \text{Questionable result}$$

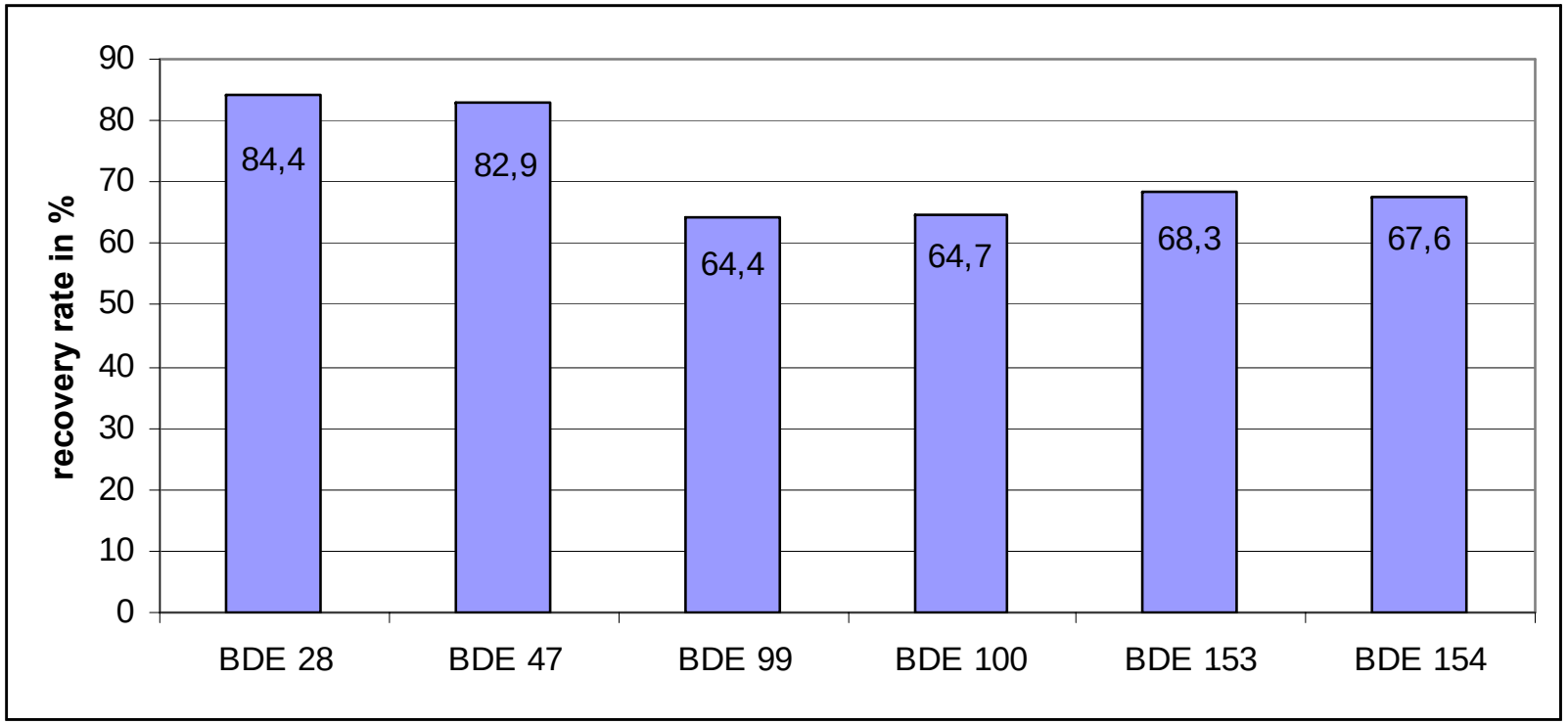
$$|\text{z-score}| \geq 3.0 \quad \text{Unsatisfactory result}$$

# Example – BDE 153, Level 1

- Details: Poster 013

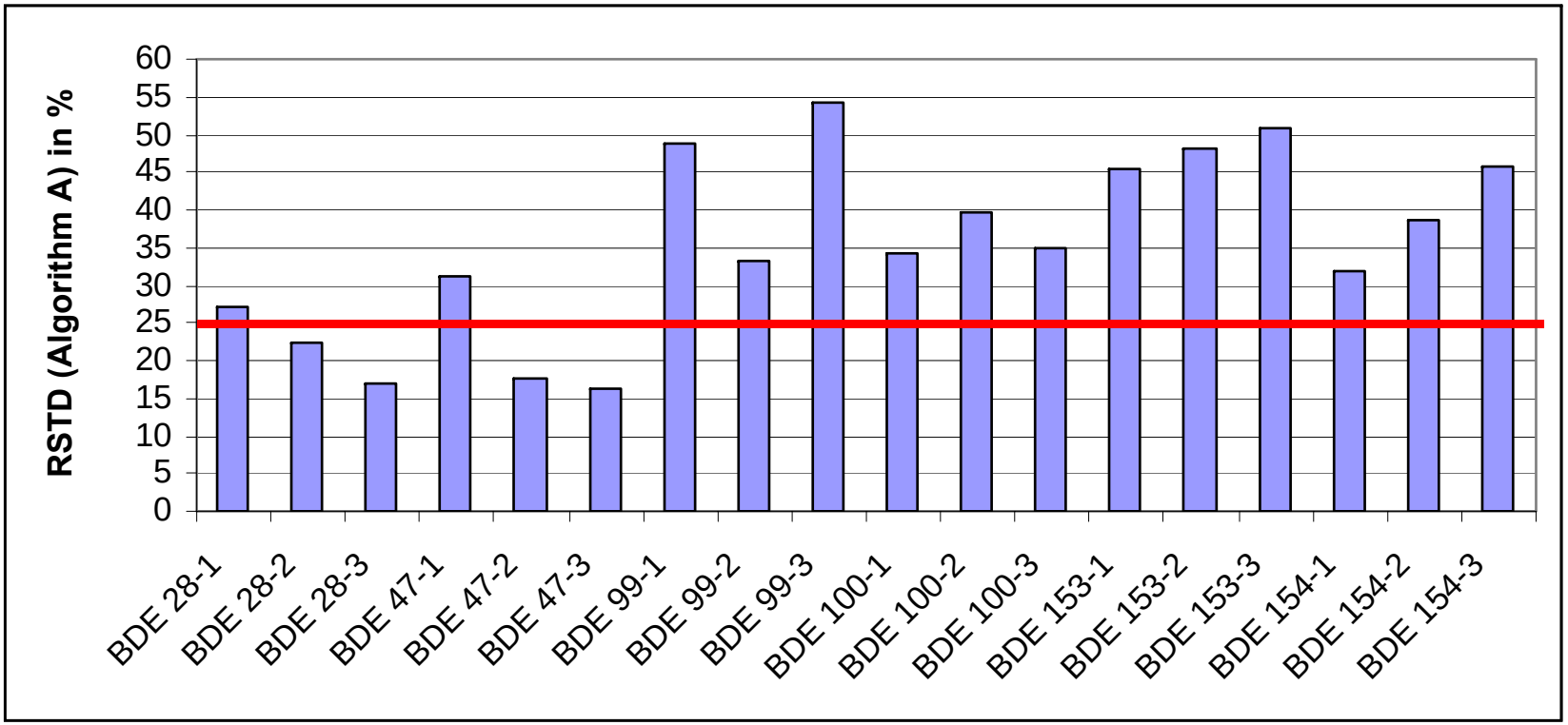


# Recovery rates



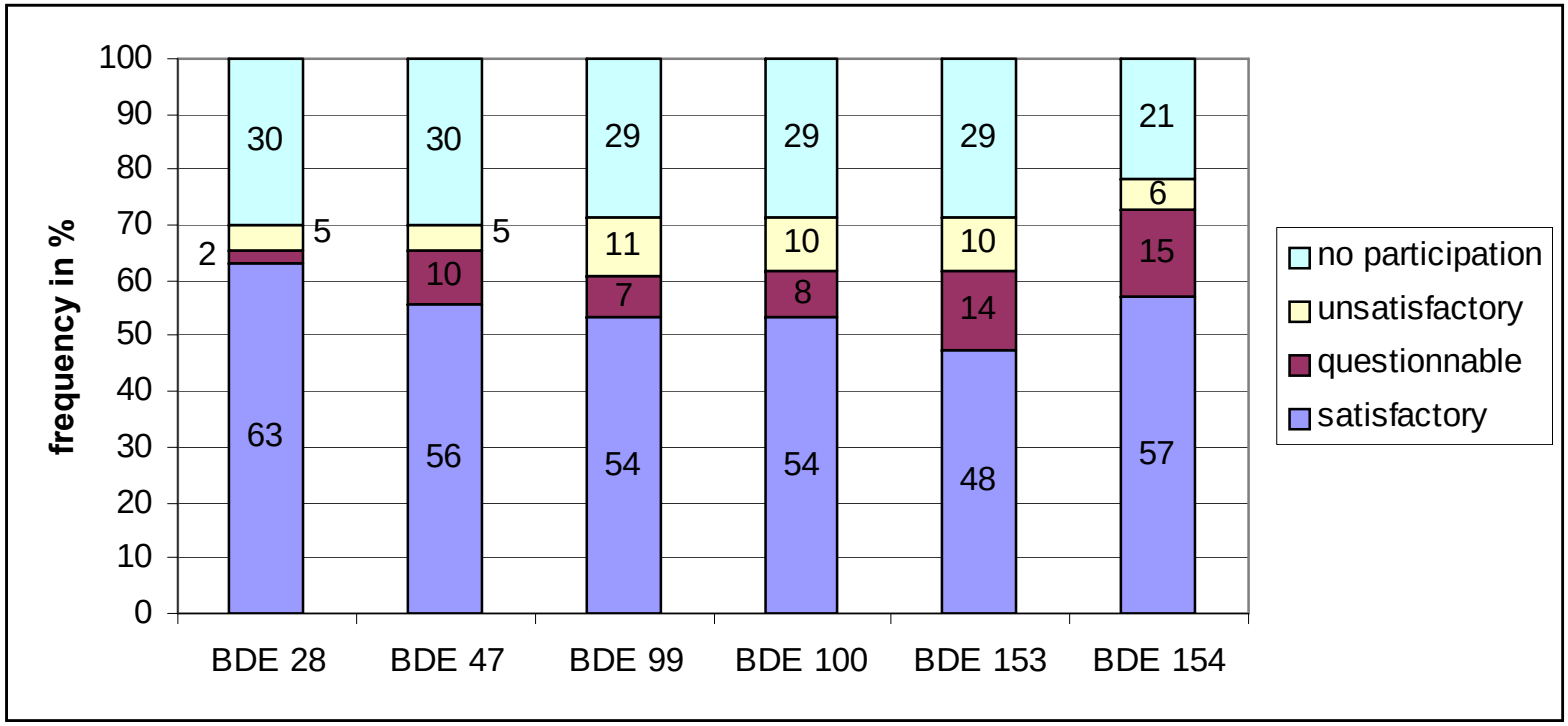

- **Reasons for low recoveries:**
  - **Incomplete extraction of Penta- and Hexa-PDBE**
    - **Due to poor method description?**
    - **Due to poor experience of labs?**
    - **Due to general problems with the extraction of non-polar compounds?**
- **Important information for the future development of methods**

# Relative standard deviation




- **Problem:**
  - **Significantly higher standard deviations for Penta- and Hexa-BDE**
    - **In some cases double as high as limited SDPA (25%)**
- **Reason:**
  - **Wide range of extraction efficiency**

# Assessment of the values




- **Number of theoretical possible values: 84**

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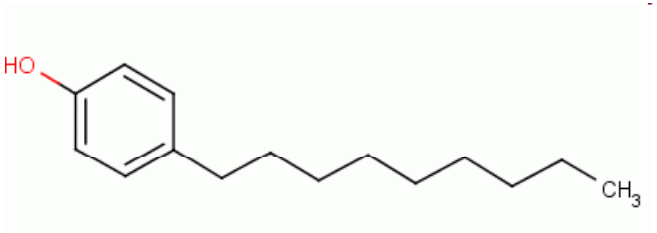
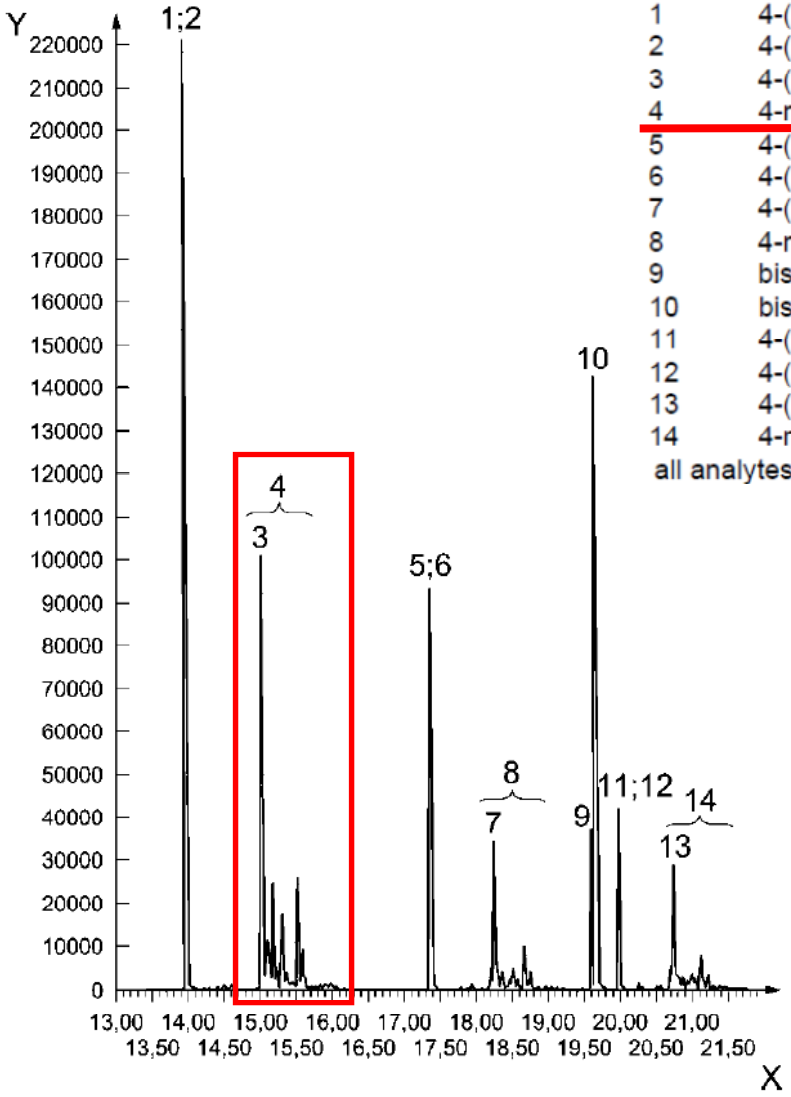
# EQS for Nonylphenols acc. to EQS Directive (2008/105/EC)

| Parameter [a)] | AA-EQS [µg/l] | Required LOQ [µg/l] |
|---|---|---|
| (24) (4-nonylphenol) **(CAS 104-40-5)** | 0,3 | 0,09 |
| (25) Octylphenol (CAS 1806-26-4) | 0,1 | 0,03 |



# 4-Nonylphenol, a mixture of isomers!




1 4-(1,1,3,3-tetramethylbutyl)phenol (OP-TMS)
2 4-(1,1,3,3-tetramethylbutyl)phenol (ring-$^{13}C_6$) (OP-$^{13}C_6$-TMS)
3 4-(3,6-dimethyl-3-heptyl)phenol (ring-$^{13}C_6$) (363 NP-$^{13}C_6$-TMS)
4 4-nonylphenol (mixture of isomers) (NP-TMS)
5 4-(1,1,3,3-tetramethylbutyl)phenol monoethoxylate ($OP_1EO$-TMS)
6 4-(1,1,3,3-tetramethylbutyl)phenol monoethoxylate (ring-$^{13}C_6$) ($OP_1EO$-$^{13}C_6$-TMS)
7 4-(3,6-dimethyl-3-heptyl)phenol monoethoxylate (ring-$^{13}C_6$) (363 $NP_1EO$-$^{13}C_6$-TMS)
8 4-nonylphenol monoethoxylate (mixture of isomers) ($NP_1EO$-TMS)
9 bisphenol A-d16 (BPA-d16-TMS)
10 bisphenol A (BPA-TMS)
11 4-(1,1,3,3-tetramethylbutyl)phenol diethoxylate ($OP_2EO$-TMS)
12 4-(1,1,3,3-tetramethylbutyl)phenol diethoxylate (ring-$^{13}C_6$) ($OP_2EO$-$^{13}C_6$-TMS)
13 4-(3,6-dimethyl-3-heptyl)phenol diethoxylate (ring-$^{13}C_6$) (363 $NP_2EO$-$^{13}C_6$-TMS)
14 4-nonylphenol diethoxylate (mixture of isomers) ($NP_2EO$-TMS)

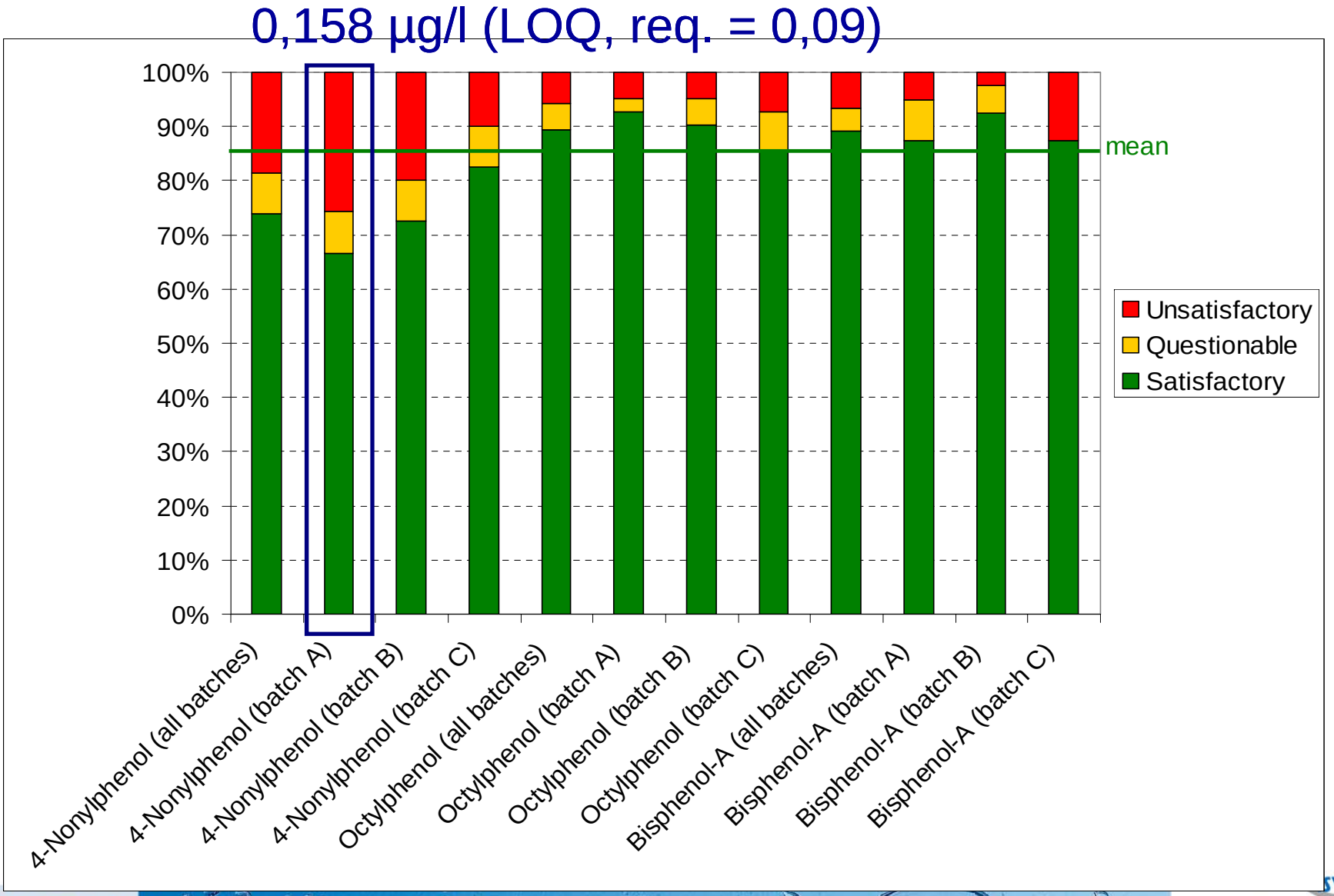
all analytes as trimethylsilyl (TMS) derivatives

# The problem of precise definitions

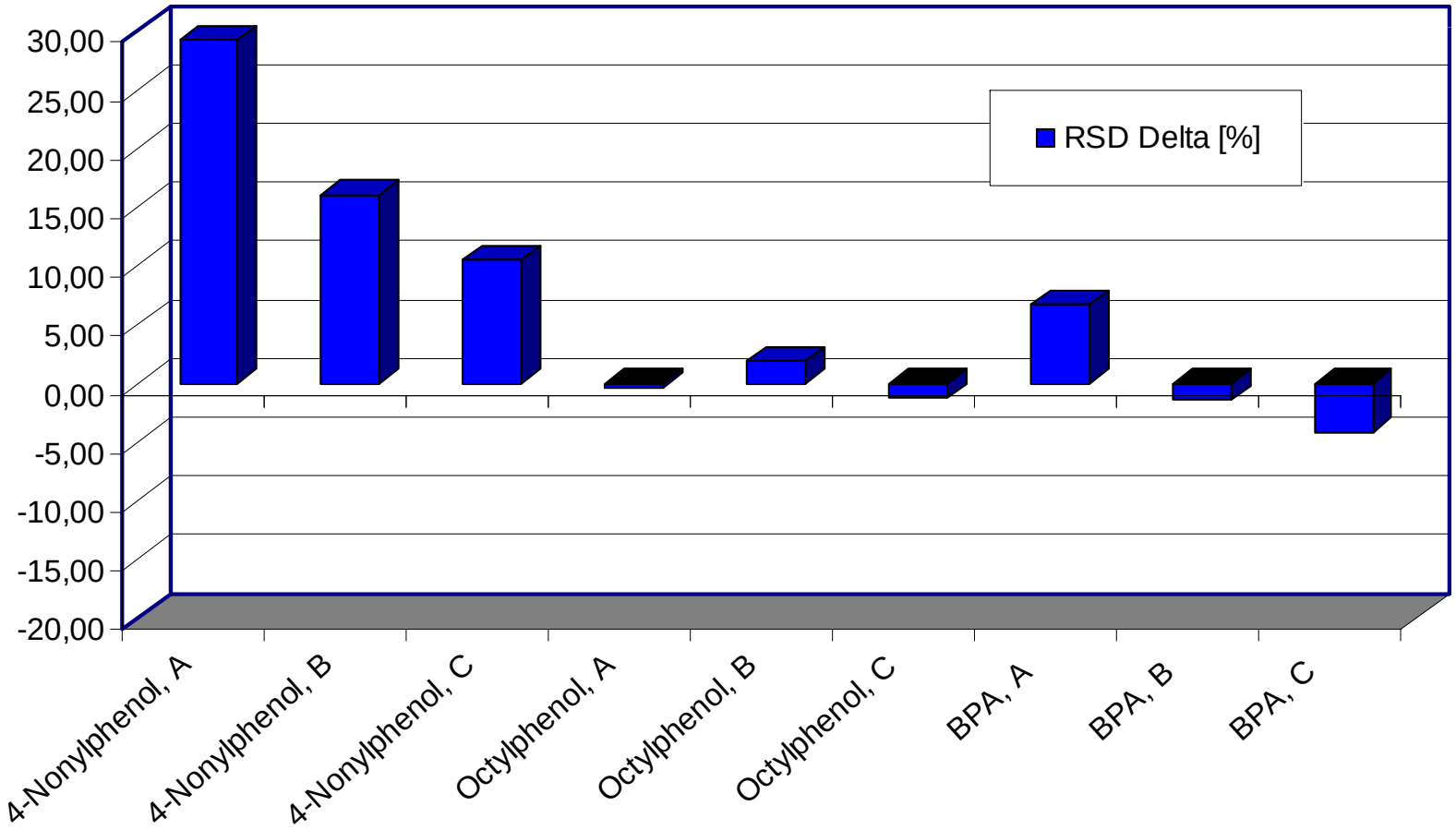
- **4-Nonylphenol**
  - 4-Nonylphenol is a mixture of branched isomers used in technical products
    - Hence, the parameter is a conventional parameter (→ sum parameter)

- **This is not fully clear in the EQS directive (DIRECTIVE 2008/105/EC)**
  - The parameter is called 4-Nonylphenol
  - The CAS number represents 4-n-Nonylphenol
    - The non-branched isomer
    - The correct CAS number reads 84852-15-3

# Assessment of the values



# Calculated RSD in comparison with the agreed SDPA (25%)



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# Conclusions

- **PTs for WFD purposes are still rare and complex**
  - Due to the high requirements (QA/QC ComDirective)
    - whole water samples (containing SPM)
    - very low concentration range
    - limited uncertainty (→ SDPA = 25%)
- **It is essential that the PT provider**
  - properly evaluates the data
  - carefully checks whether the reference value can/has to be used
  - contributes to the enhancement of the methods
- **Specific problems with conventional parameters (sum parameters) have to be addressed**
  - in the communication with participants
  - to the authorities (legislators)

# Many thanks to the co-operating PT providers