Network of reference laboratories and related organisations for monitoring and bio-monitoring of emerging environmental pollutants

Experience from the NORMAN Validation Trials on the Analysis of DecaBDE

The views expressed are purely those of the writer and may not under any circumstances be regarded as stating an official position of the European Commission

NORMAN Contract 018486 - FP6 - Priority 6.3

Objectives

- **Developing a harmonised method validated at routine level for a selected emerging pollutant (decaBDE)**
- **Applying the protocol developed in WP Validation**
- **Giving feedback to sub-projects SEARCH, NETWORK and VALIDATION**

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1st Meeting
Discussion of Critical Factors

First Round with
Expert Laboratories

Transfer of
Knowledge

2nd Meeting/Training
Advice on all critical factors

Second Round with
Routine Laboratories

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1st Interlaboratory Comparison organised by UBA in 2006

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1st Interlaboratory Comparison

- **Objective**
  - Demonstrate that the method is under control in expert laboratories
  - Harmonize the procedure for the second round
- **Samples**
  - NIST SRM 2585 - Organic Contaminants in House Dust [BDE 209] = 2510 +/- 190 µg/kg
  - GC test solution of undisclosed concentration
- **Assessment**
  - Statistical evaluation of results using various approaches
    - ISO 5725
    - Robust statistics
- **Conclusion**
  - Modification of the analytical protocol according to the results

Participating Laboratories

CSIC, Barcelona, Spain

CIEMAT, Madrid, Spain

INERIS, Paris, France

ITM, Stockholm, Sweden

JRC-IES, Ispra, European Commission

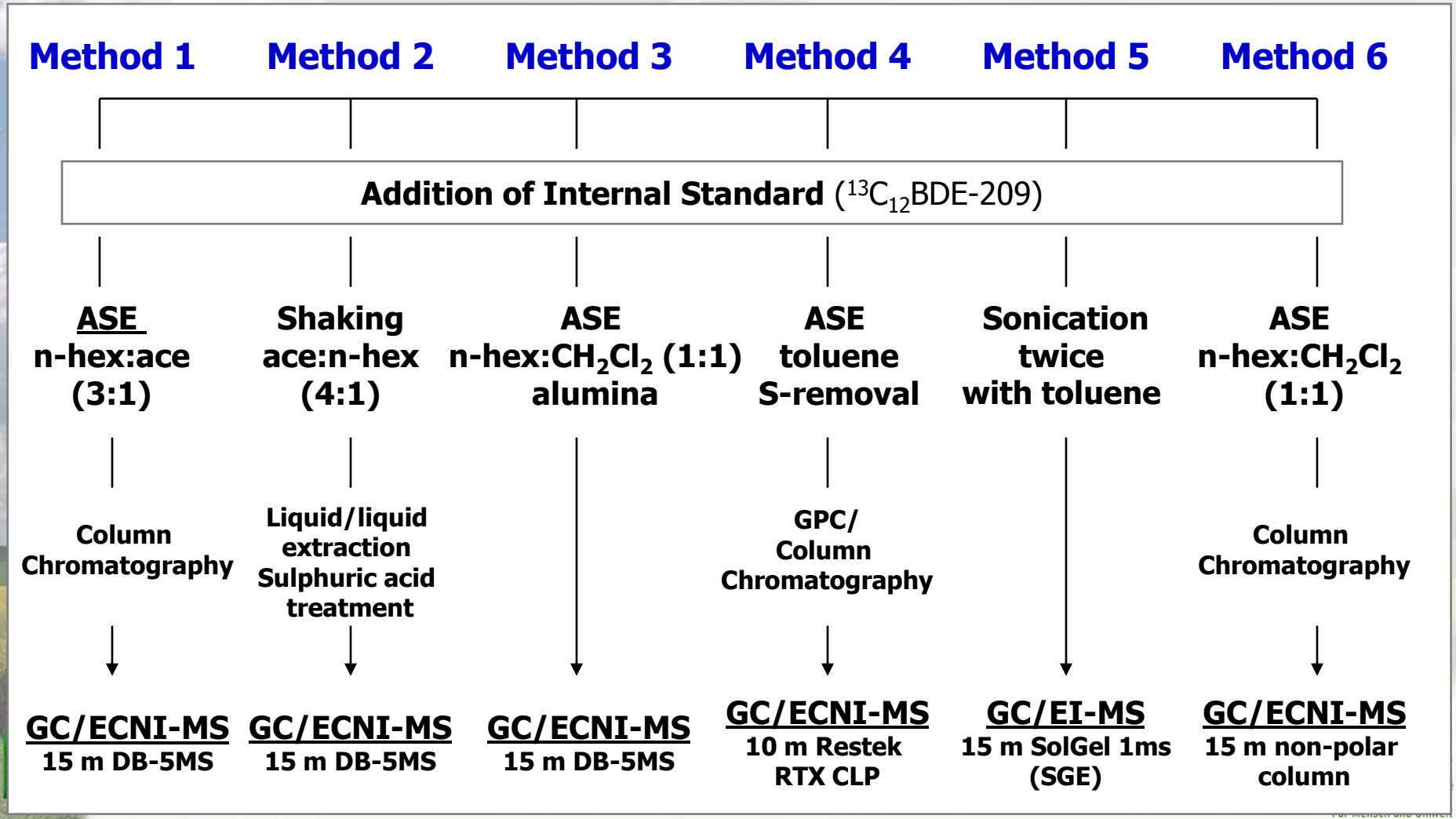
UBA, Berlin, Germany

Methodology

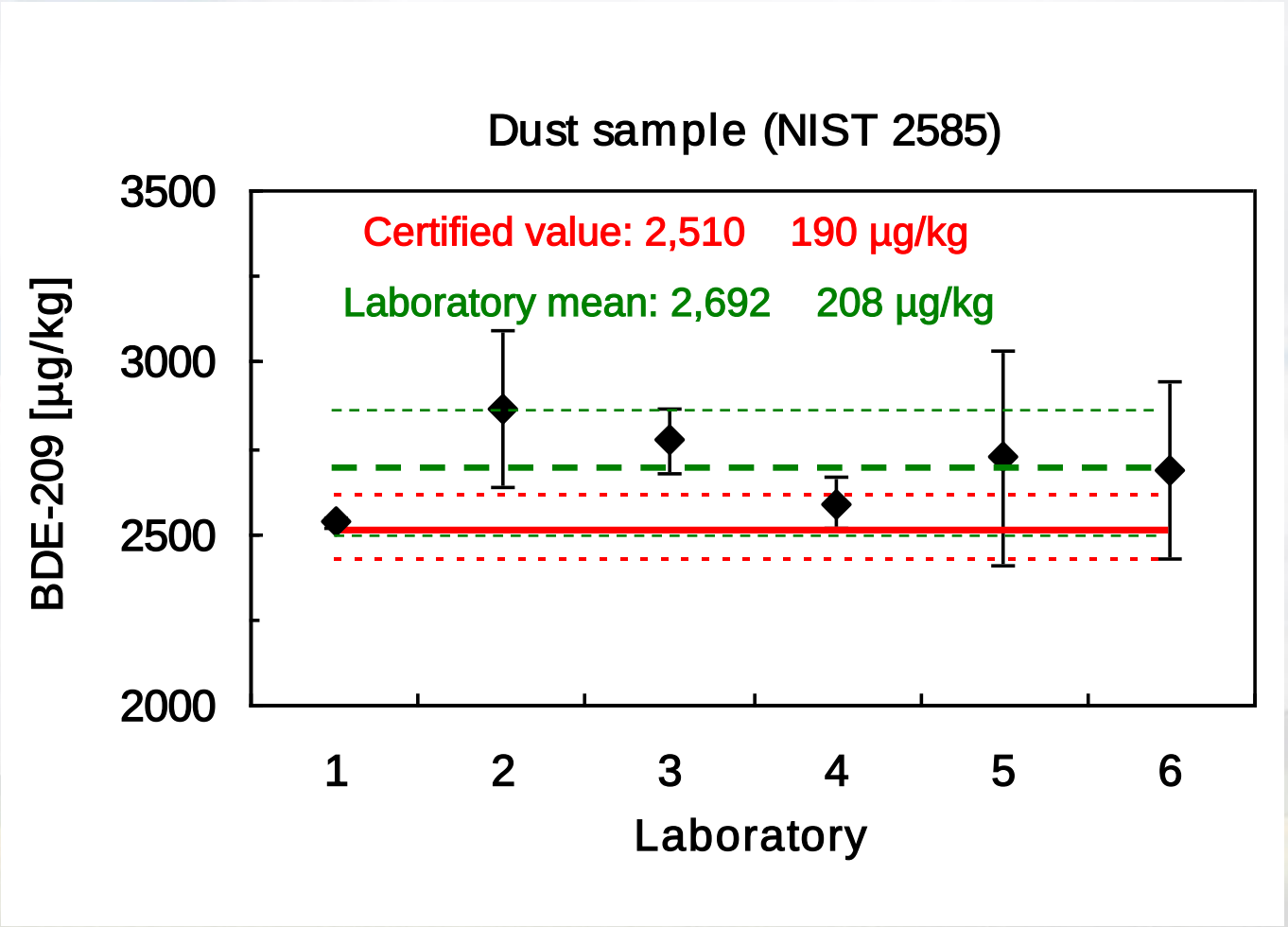
- **Any appropriate analytical methodology was allowed to be used**
  - **4 replicate analyses of samples**
  - **4 independent blank replicates**
  - **Use of $^{13}C_{12}$-labelled decaBDE as IS obligatory**
  - **Short and narrow GC column (<15 m, <0.25 mm I.D.)**
  - **Short residence time in the injector/moderate temperature**
  - **Measures to prevent photochemical degradation**
- **Statistical evaluation of results using the software ProLab (QuoData Ltd., Dresden, Germany)**
  - **According to ISO 5725-2 and DIN 38402-42, respectively**
- **Modification of the analytical protocol according to the results obtained**

Analytical Procedures

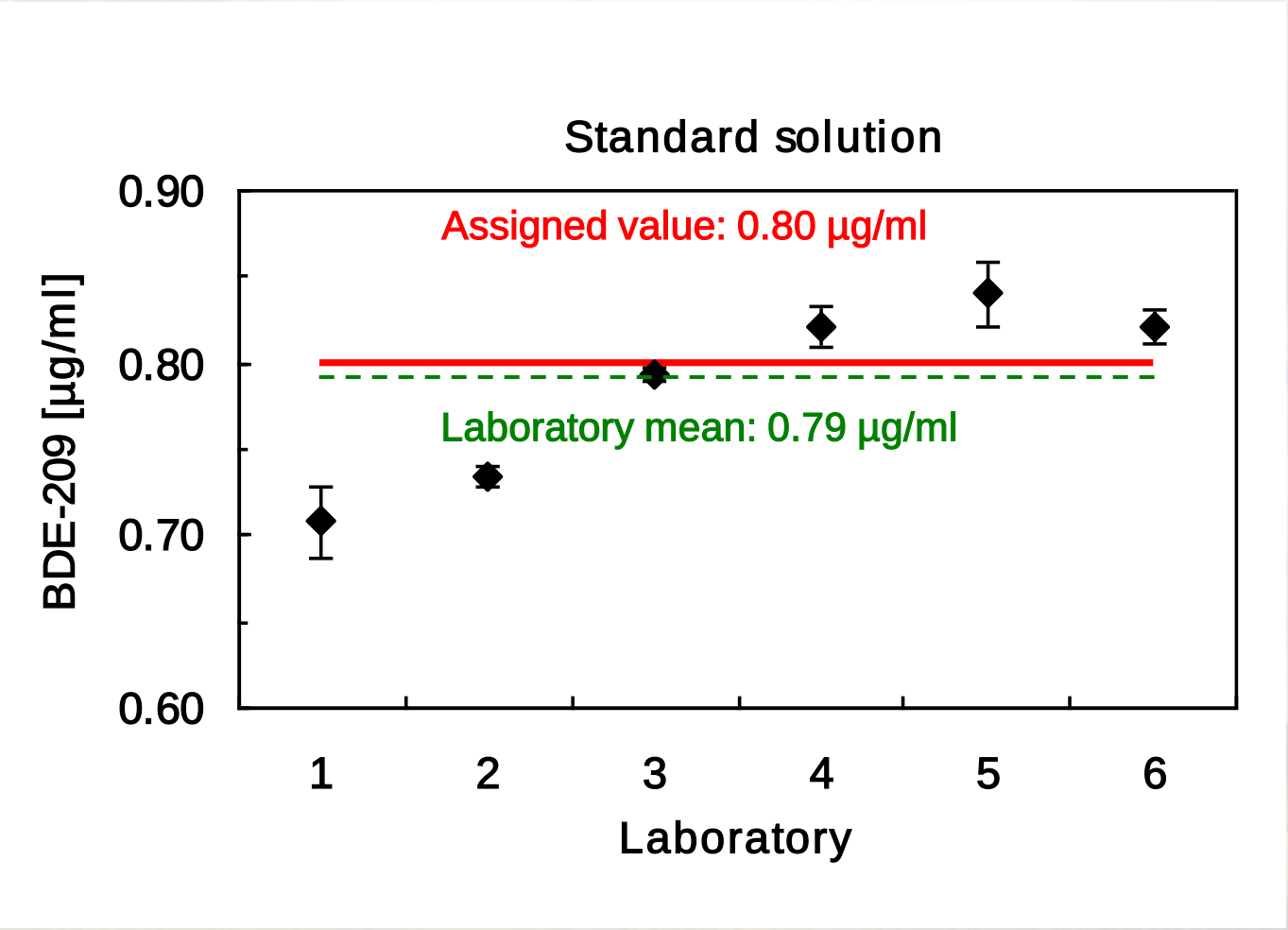
Dust sample (NIST 2585) (4 replicates) | **Standard Solution** (4 replicates) | **Blank** (4 replicates)



Results – 1st ILC



Results – 1st ILC



Results – 1st ILC

Sample	l	n	n_{AP}	$\overline{x}$	s_R	CV_R	s_r	CV_r
Dust	**6**	**24**	**8.3**	**2,692**	**207.7**	**7.7**	**203.8**	**7.6**
Solution	**6**	**24**	**0**	**0.79**	**0.05**	**6.9**	**0.01**	**1.7**

l	Number of laboratories
n	Number of individual results
n_{AP}	Percentage of outliers
$\overline{x}$	Total mean after elimination of outliers [µg/kg or µg/ml]
s_R	Reproducibility standard deviation [µg/kg or µg/ml]
CV_R	Reproducibility variation coefficient [%]
s_r	Repeatability standard deviation [µg/kg or µg/ml]
CV_r	Repeatability variation coefficient [%]

Conclusion – 1st ILC

- **Apparently, the choice of the analytical method is less important than**
  - **Experience of the laboratories**
  - **Careful control of all critical factors (thermal and photochemical degradation, adsorption to surfaces, blanks)**

2nd Interlaboratory Comparison organised by IVM in 2008

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2nd Interlaboratory Comparison

- **Objective**
  - Validate the harmonized procedure
  - Validated method for the determination of decaBDE in environmental samples at routine level
- **Samples**
  - NIST SRM 2585 - Organic Contaminants in House Dust
  - Marine sediment
  - GC test solution of undisclosed concentration
- **Assessment**
  - Statistical evaluation of results using various approaches
    - ISO 5725
    - Robust statistics
- **Conclusion**
  - Modification of the analytical protocol according to the results, where appropriate

Participating Laboratories

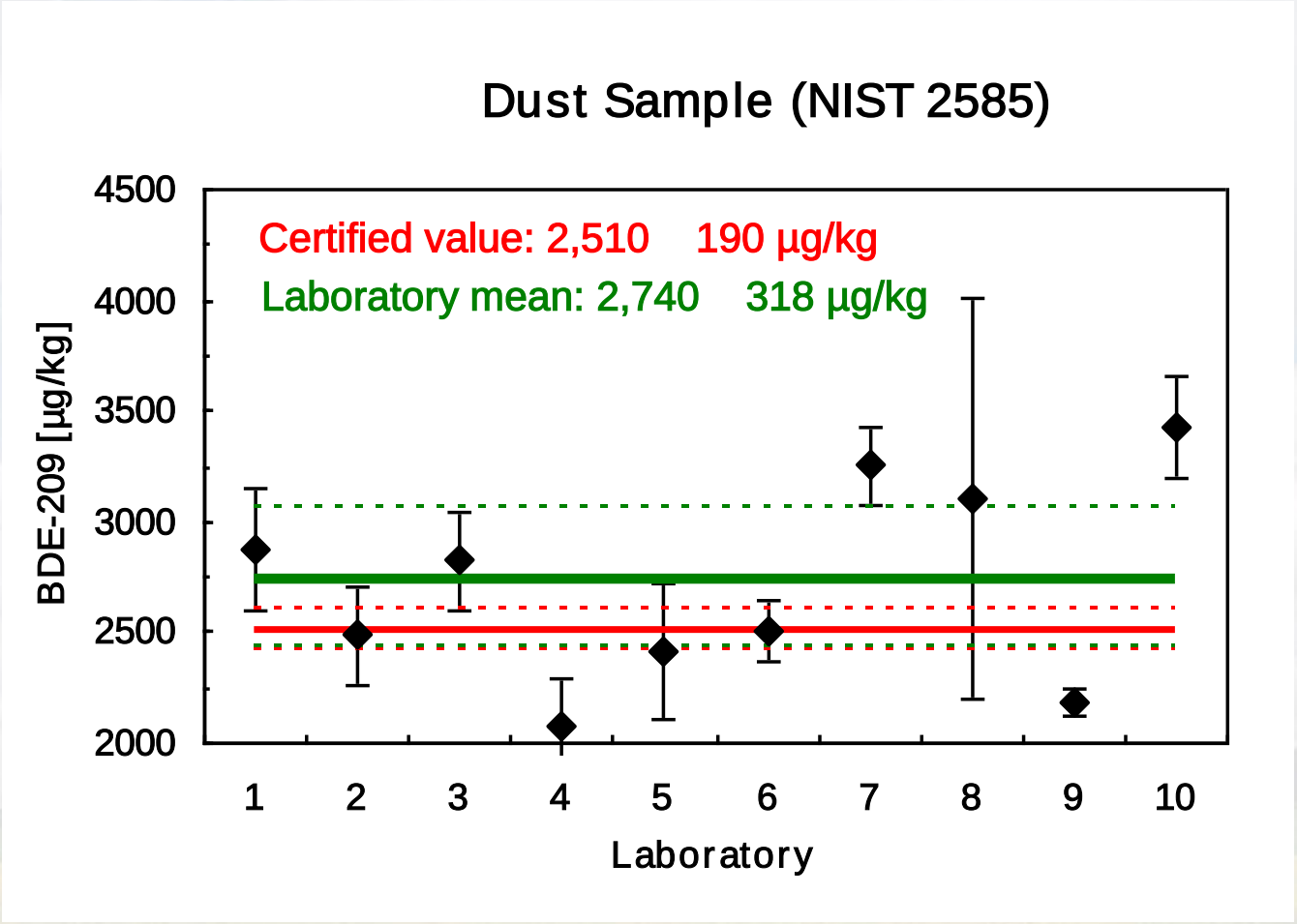
Institute of Chemical Technology, Prague, Czech Republic
CEFAS, Essex, UK
University of Siena, Italy
Applus+ LABAQUA, Alicante, Spain
Unilever, UK
University of Antwerp, Wilrijk, Belgium
Waterdienst, Lelystad, Netherlands
IVM, Amsterdam, The Netherlands
LANUV, Düsseldorf, Germany
EMPA, Dübendorf, Switzerland
Department of Innovation, Industry, Science and Research, Pymble, Australia
Ministry of the Environment, Ontario, Canada

Analytical Procedures

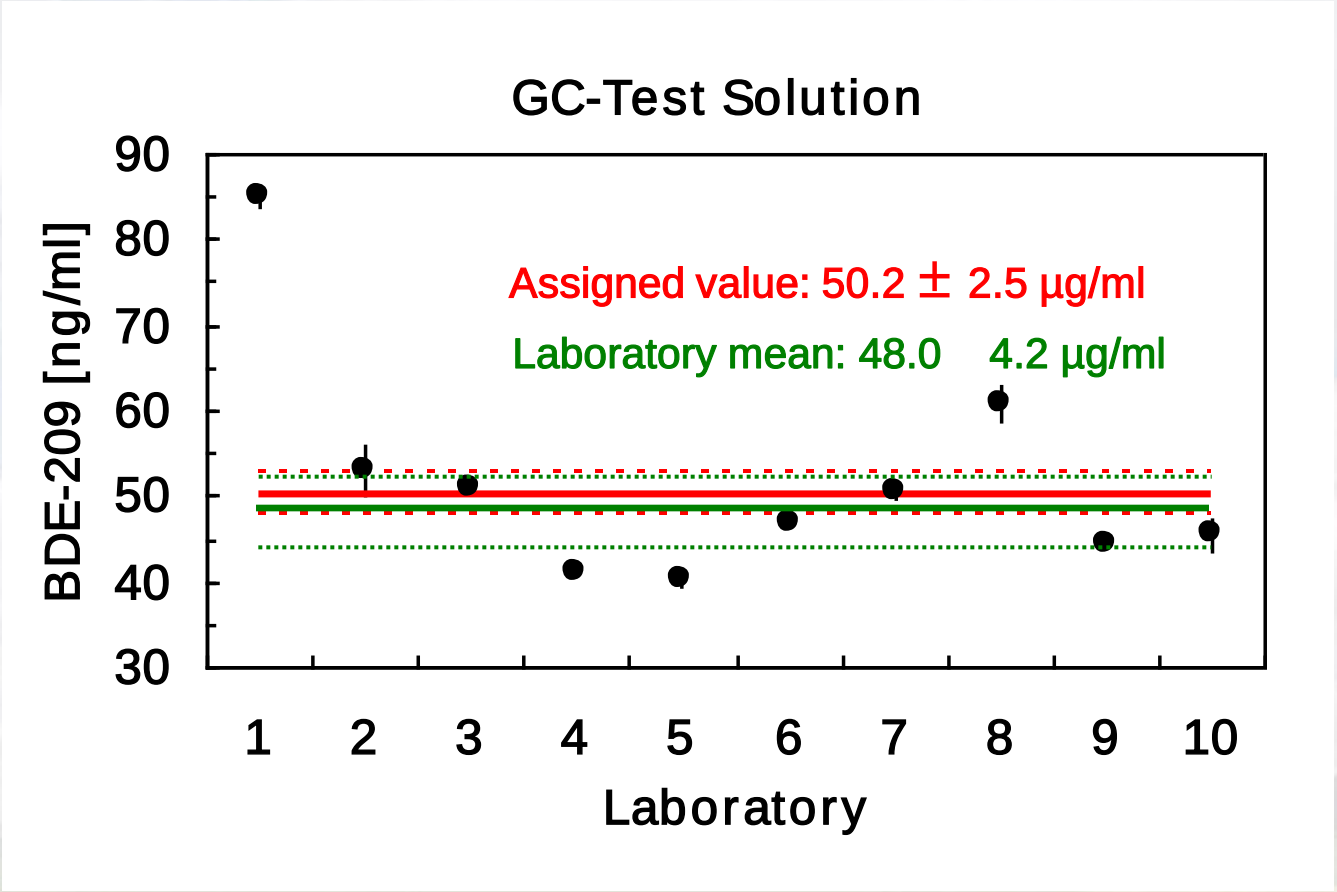
Reported by 10 Laboratories

Extraction	**ASE (2)** **Soxhlet (5)** **Hot soxhlet (2)** **Sonication (1)**
Clean-up	**Column chromatography (8)** **GPC (2)**
Analysis	**GC/EI-LRMS (1)** **GC/EI-HRMS (2)** **GC/ECNI-LRMS (5)** **GC/ECNI-HRMS (2)**

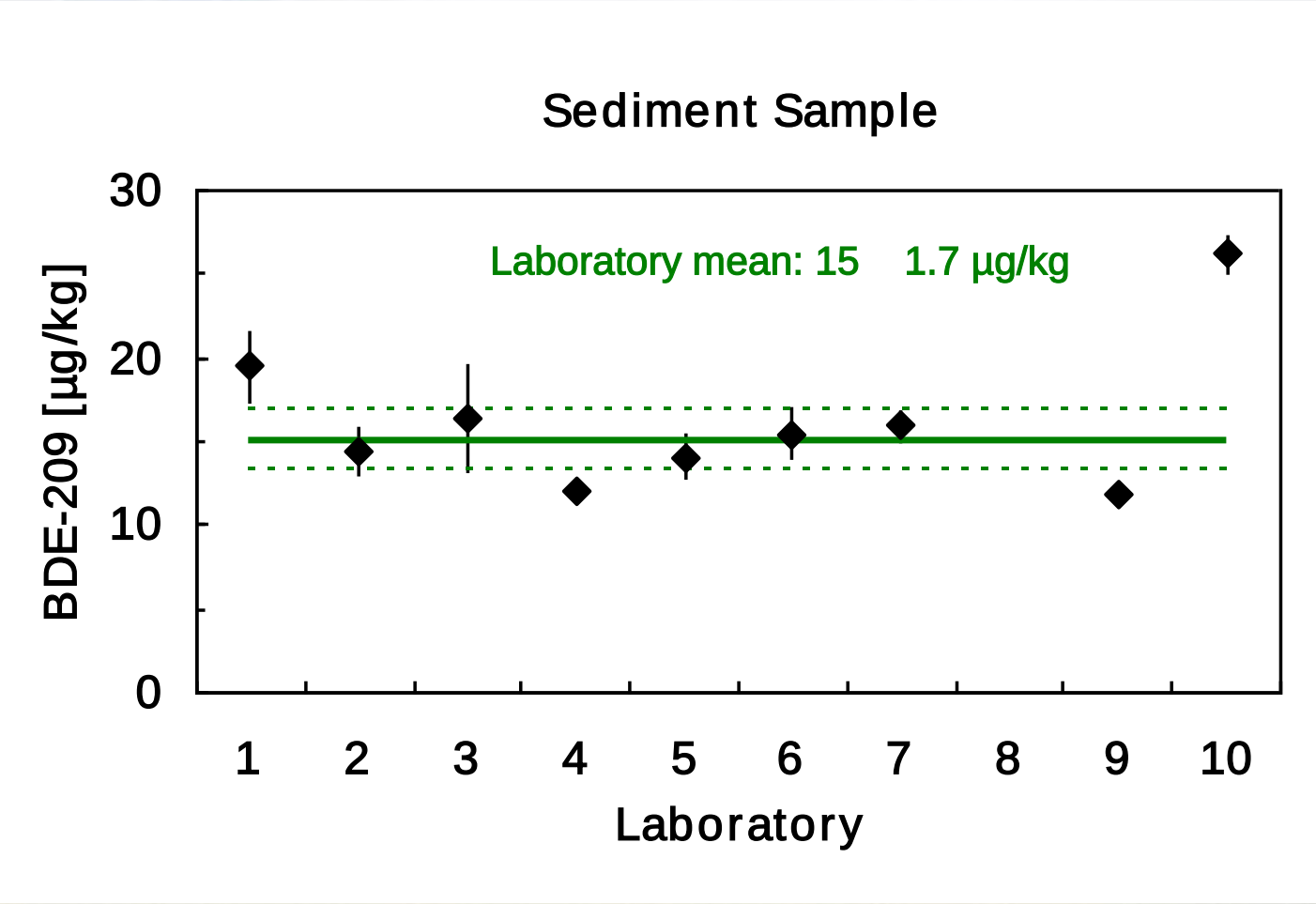
Results – 2nd ILC



Results – 2nd ILC



Results – 2nd ILC



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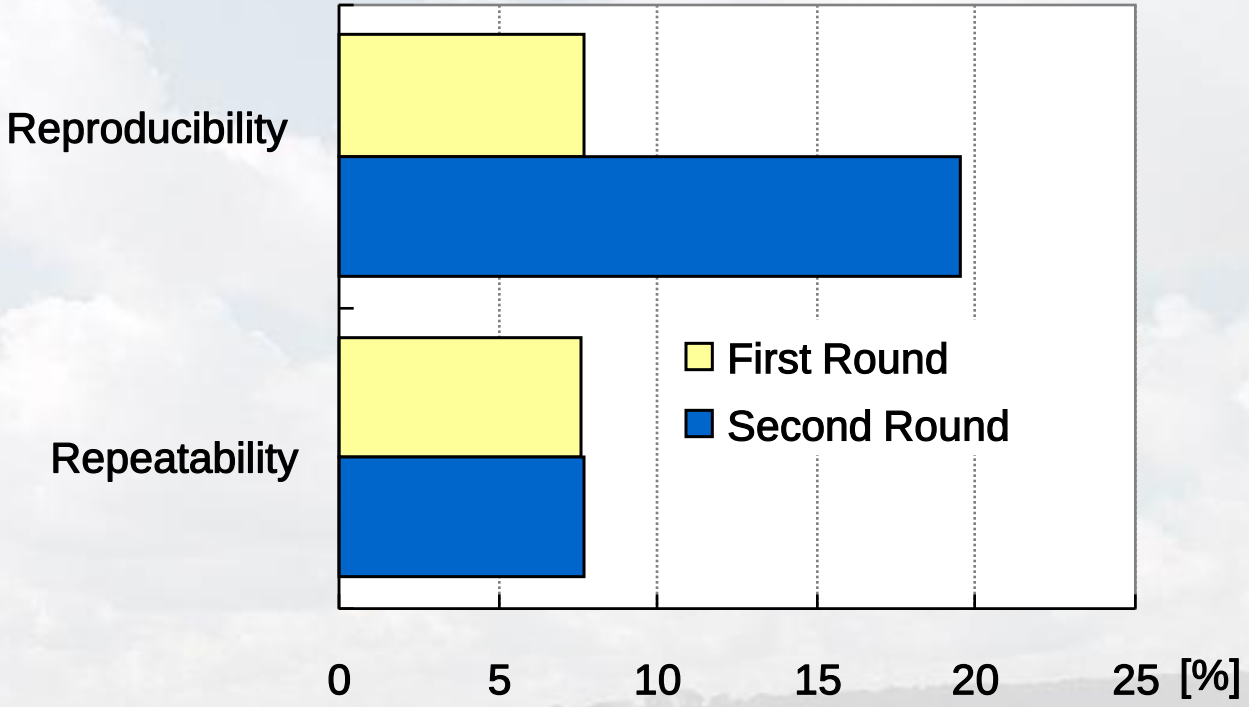
Results – 2nd ILC

Sample	l	n	n_{AP}	$\overline{x}$	s_R	CV_R	s_r	CV_r
Dust	**10**	**39**	**2.5**	**2,740**	**536**	**19.5**	**212**	**7.7**
Sediment	**9**	**32**	**11.1**	**15**	**2.9**	**19.4**	**1.8**	**11.9**
Solution	**10**	**36**	**10**	**48**	**6.5**	**13.6**	**1.7**	**3.6**

l	Number of laboratories
n	Number of individual results
n_{AP}	Percentage of outliers
$\overline{x}$	Total mean after elimination of outliers [µg/kg or µg/ml]
s_R	Reproducibility standard deviation [µg/kg or µg/ml]
CV_R	Reproducibility variation coefficient [%]
s_r	Repeatability standard deviation [µg/kg or µg/ml]
CV_r	Repeatability variation coefficient [%]

Comparison of Results



Conclusion (1)

- **Several methods for extraction and clean-up are appropriate for the analysis of decaBDE in dust as well as in sediment**
- **Apparently, the choice of the analytical method is less important than**
  - **the experience of the laboratories and**
  - **the careful control of critical factors (thermal and photochemical degradation, blanks)**
- **Optimisation of GC conditions and proper QA/QC measures are of utmost importance**
- **The use of $^{13}C_{12}$-BDE-209 as internal standard is compulsory to compensate for the losses throughout the entire analytical procedure**

Conclusion (2)

- **Routine laboratories were able to analyse decaBDE in environmental samples with acceptable accuracy**
  - **Reproducibility better than in recent QUASIMEME ILC**
- **Laboratory performance in the analysis of emerging contaminants at the routine level can be improved by transfer of knowledge from expert to routine laboratories via**
  - **Workshops**
  - **Harmonised analytical protocols**
  - **Proper training activities**