Euramet Project 924

PTB

"Development of a sustainable traceability and dissemination system providing Europe-wide comparable measurement results in water monitoring under the WFD (2000/60/EC)"

Organized by
PTB, BAM, LNE and IRMM

Background

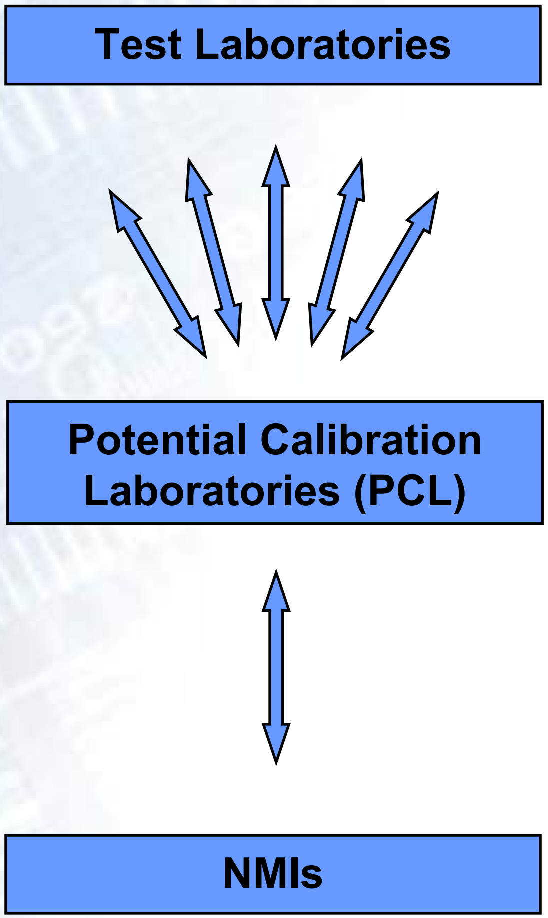
WFD:

- Good quality of surface, ground and coastal water in the EU by 2015
- Environmental Quality standards (c_{EQS} (Hg) = 50 ng/l)
- List of priority substances (Ni, Cd, Pb, Hg)
- Measurement methods for monitoring and assessment of the water quality:„..will ensure the provision of data of an equivalent scientific quantity and **comparability**“ (Annex V, 1.3.6)

Project objectives:

- Metrological dissemination structure providing:
  - Sustainability
  - Link with all monitoring laboratories
  - Europe-wide comparable measurement results

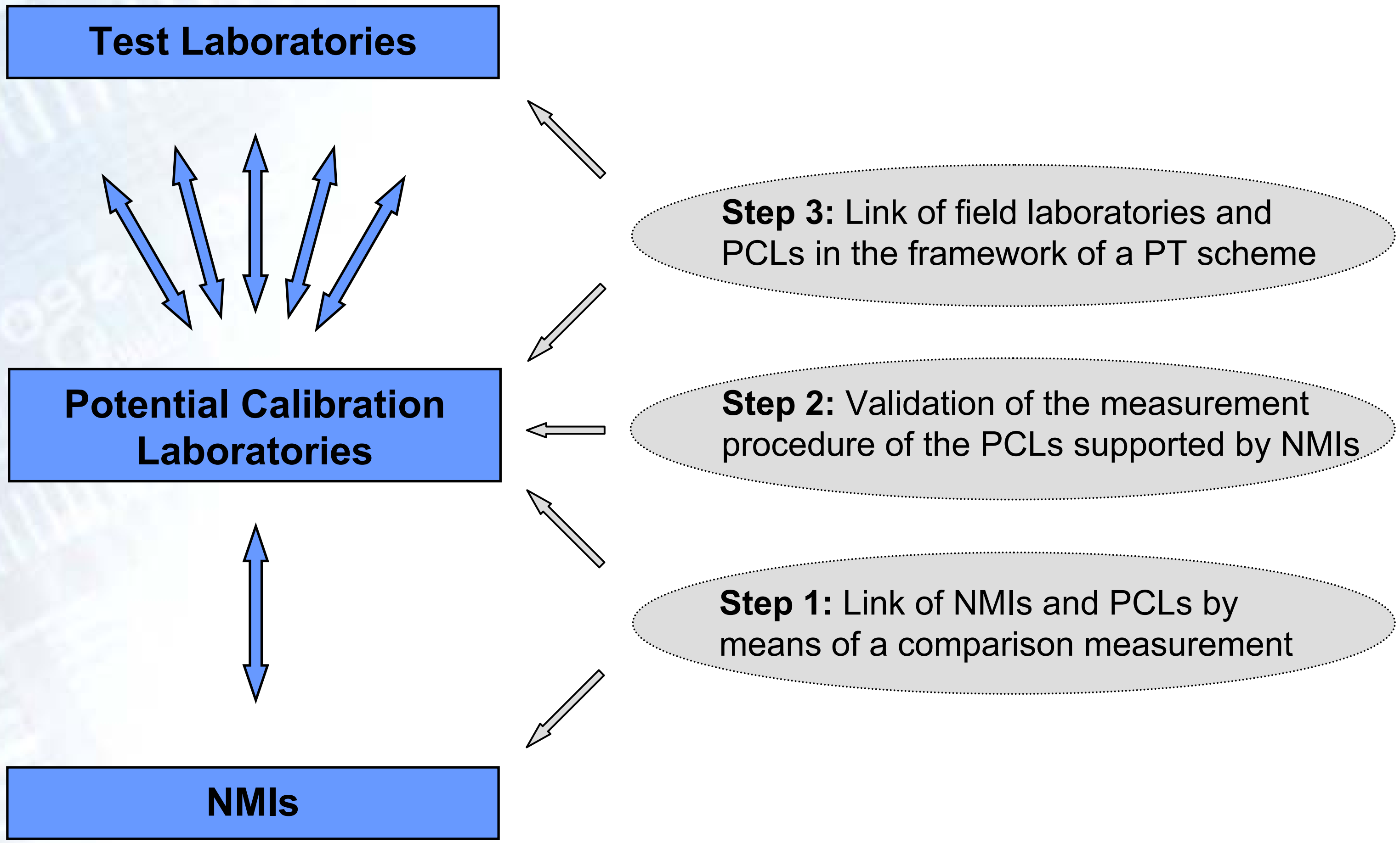
Planned dissemination structure



Basic approach:
- Use of existing QS
- Enable PCLs to provide traceable RV

Advantages:
- Minimum changes
- Best chances to be accepted
- All test laboratories are reached
- Mulitiplier function of the PCLs
- Discharge of the NMIs
- Sustainable

Planned dissemination structure



PCL: Potential Calibration Laboratories

Step 1: Comparison NMIs / PCLs

Part 1 (CCQM-P100.1)

- **Pure water**
- Prepared by BAM
- Gravimetrically spiked
- Gravimetrical reference value
- Concentration 0,02 - 0,1 µg/l

Part 2 (CCQM-P100.2)

- **Natural water**
- Prepared by LNE
- Water filtered
- Gravimetrical reference value only for Hg
- Concentration 0,2 - 1,0 µg/l

Measurements completed

List of participants

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Germany:	**PTB, BAM** IWW, Ifu Bayern, LUA NRW, IHU HH, Lvua SH, Hlug HE, Tlug TH
France:	**LNE** CEMAGREF, INERIS, BRGM, IFREMER
Sweden:	**SP** NIVA (No),SYKE(Fi)
Europe:	**IRMM**
Romania:	**INM**
Bulgaria:	**NCM**
UK:	**LGC** (P100.2)
Canada:	**NRC** (P100.2)
Mexico:	**CENAM**
Chile:	**CQM**
USA:	**NIST** (P100.2)
Hungary	Ultuki
Italy	APAT
Austria	UBA
Israel	WML, Phlta
Portugal	INSA, INETI

CCQM:	12 NMIs	+ 3 non-NMIs
EURAMET:	7 NMIs	+ 17 non-NMIs

Σ 32 laboratories from 19 countries

Mercury (pure water samples)

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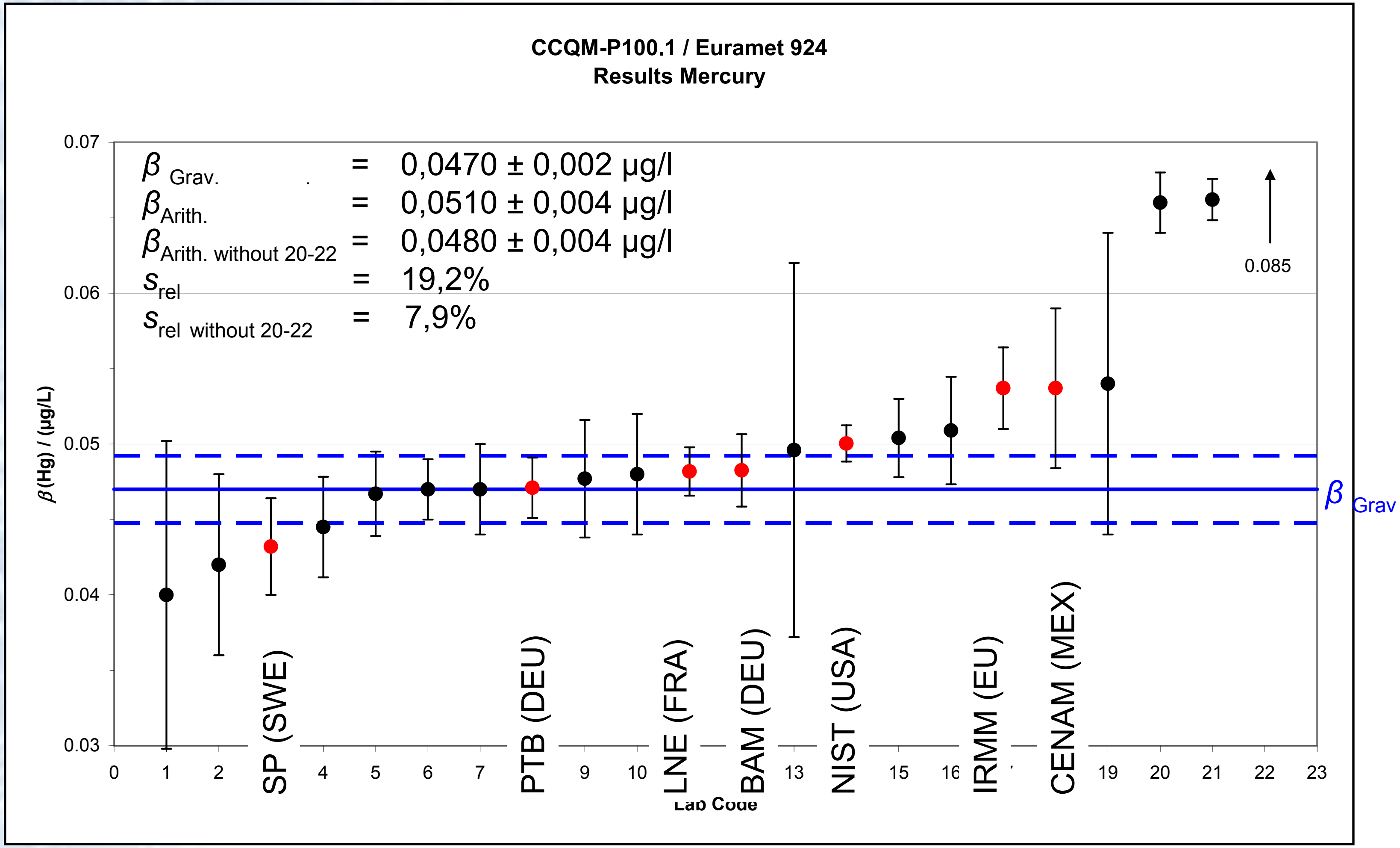

Gravimetrical value (Hg)

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$$\beta = (0{,}04699 \pm 0{,}00224)\ \mu g/l$$

$$\beta = (\beta_{gravimetry} + \beta_{matrix}) \pm U$$

$$U = 2 \cdot (u^2_{gravimetry} + u^2_{matrix\ measurement} + u^2_{stability})^{0,5}$$

$\beta_{gravimetry}$	=	0,04549 µg/l
β_{matrix}	=	0,00150 µg/l
$u_{gravimetry}$	=	0,00083 µg/l
$u_{matrix\ measurement}$	=	0,00075 µg/l
$u_{stability}$	=	0,00084 µg/l

Mercury (mean values)

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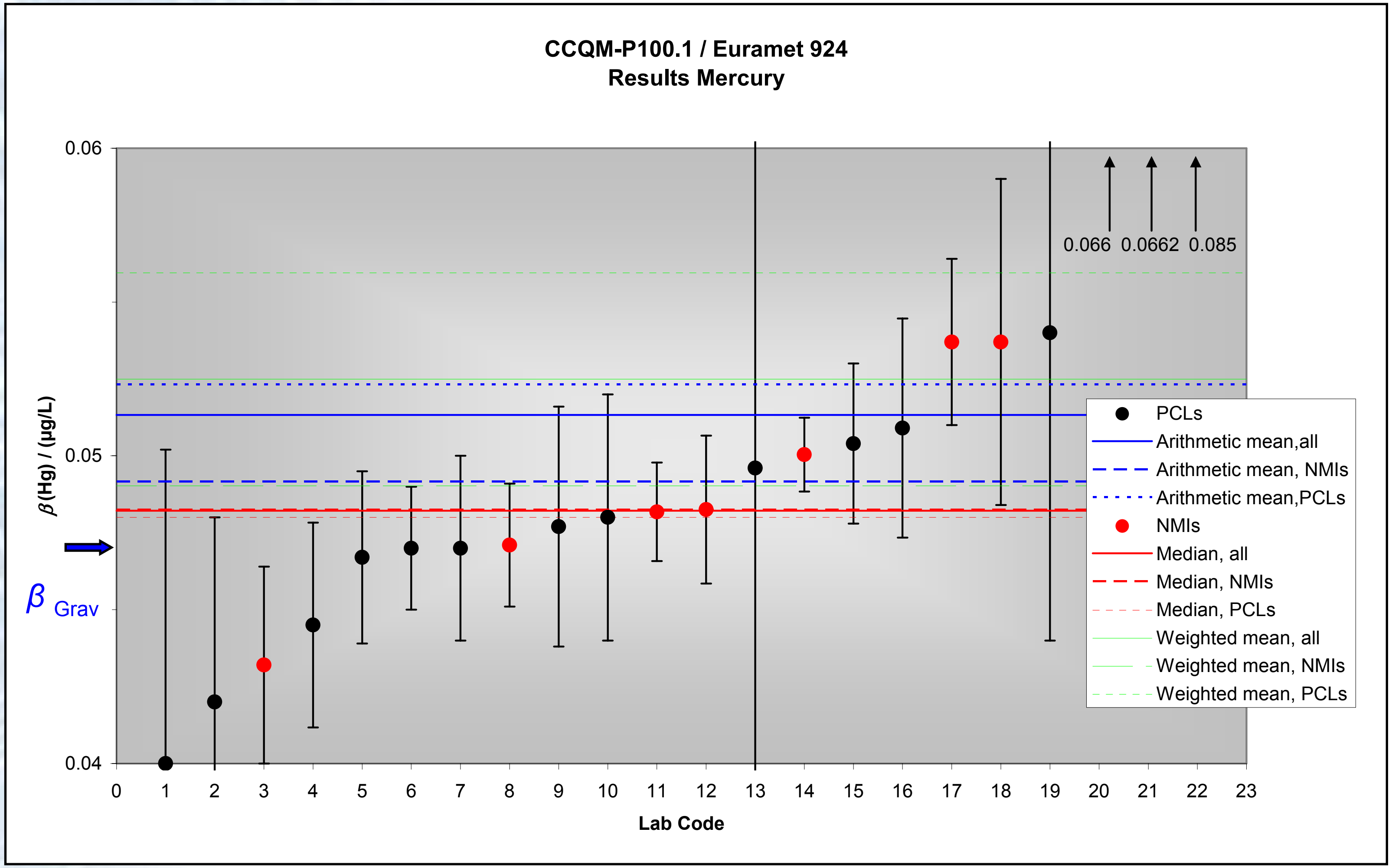
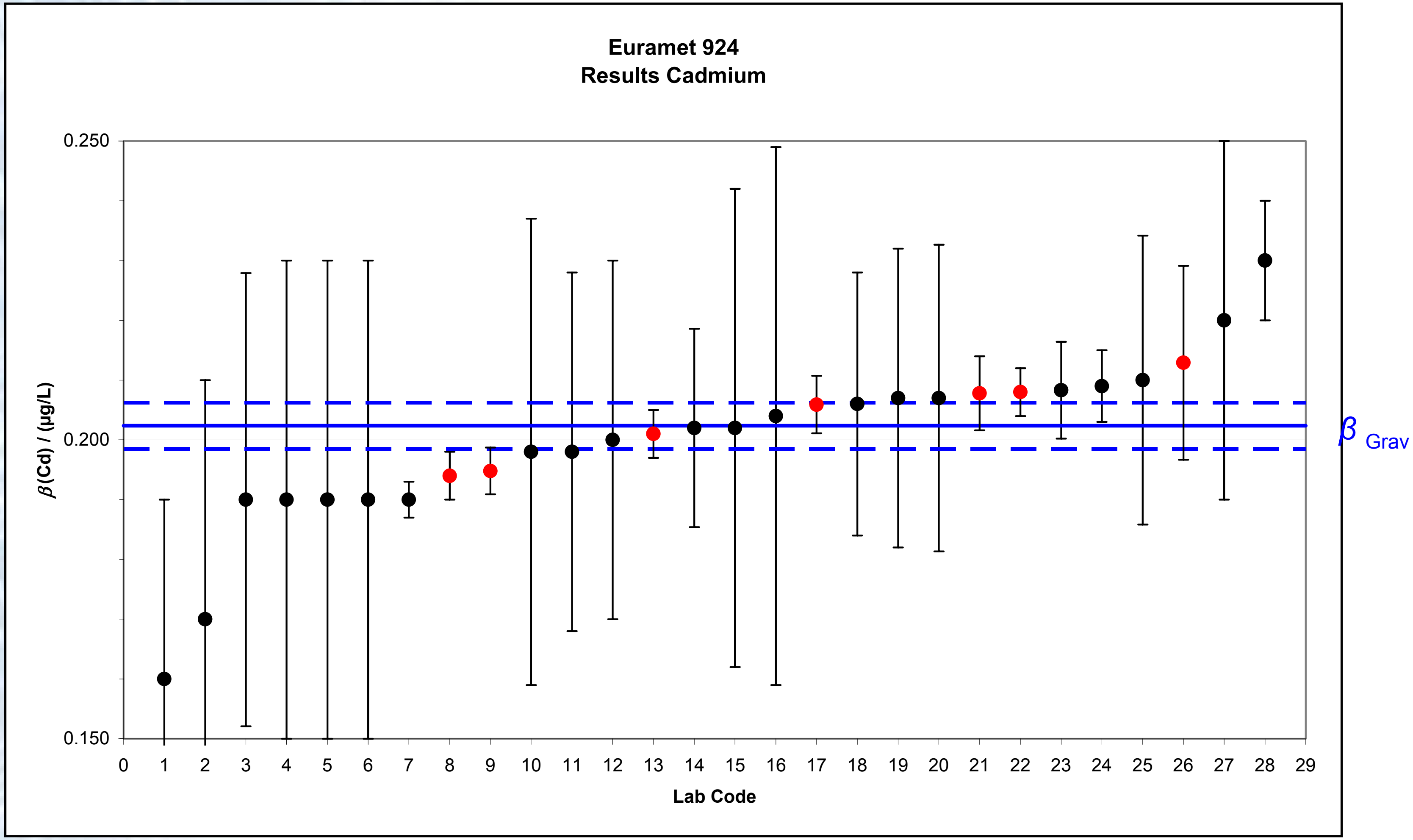


Cadmium (pure water samples)

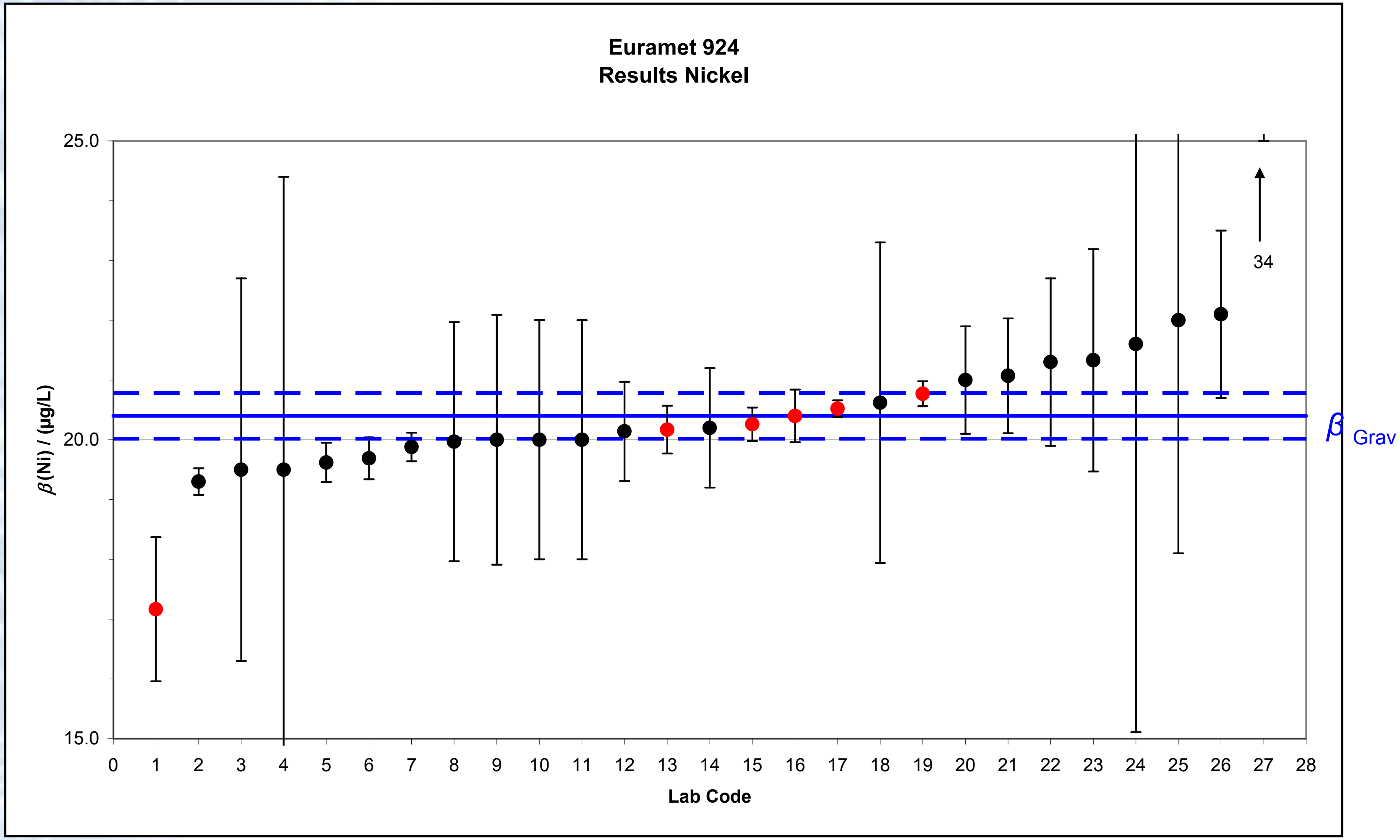


β_{Grav} = 0,2024 ± 0,0050 µg/l

$\beta_{\text{Arith. mean}}$ = 0,2002 ± 0,0052 µg/l

s_{rel} = 6,9 %

Nickel (pure water samples)



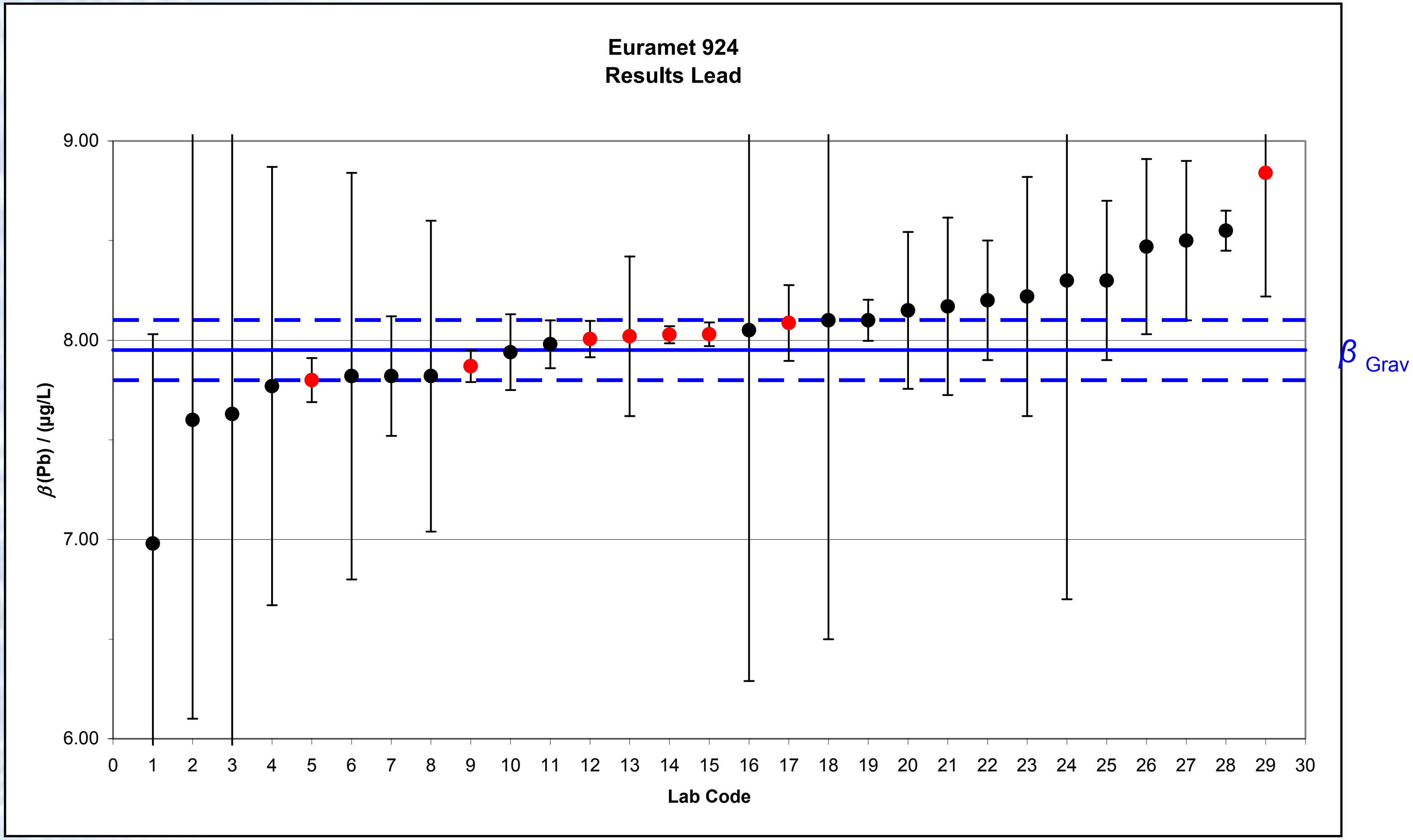
$\beta_{\text{Grav.}}$ = 20,40 ± 0,40 µg/l

$\beta_{\text{Arith. mean}}$ = 20,82 ± 1,08 µg/l

s_{rel} = 13,5 %

$s_{\text{rel without 27}}$ = 4,9%

Lead (pure water samples)



$\beta_{\text{Grav.}}$	= 7,951 ± 0,304 µg/l
$\beta_{\text{Arith. mean}}$	= 8,04 ± 0,13 µg/l
s_{rel}	= 4,3 %

Mercury (natural water samples)

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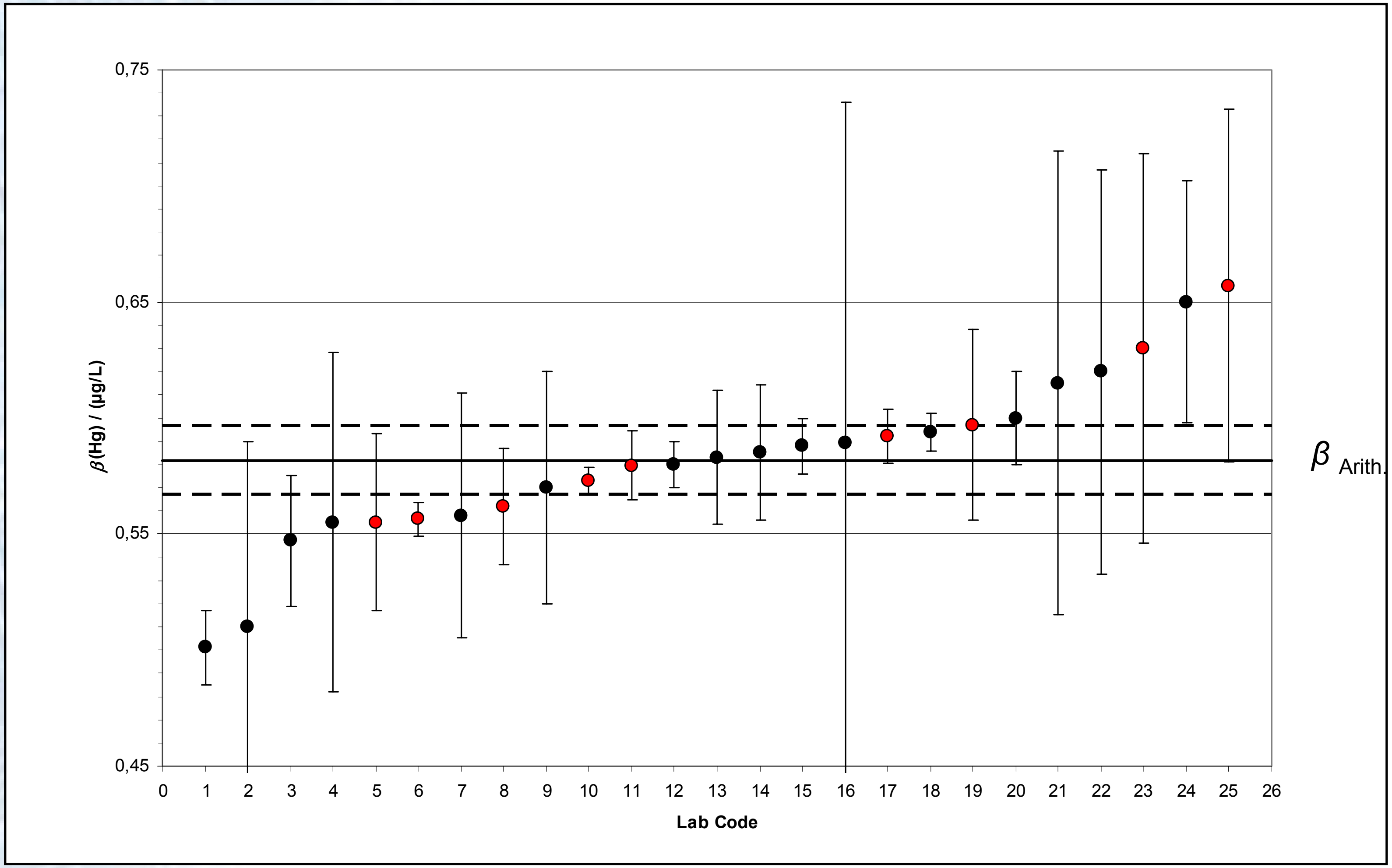
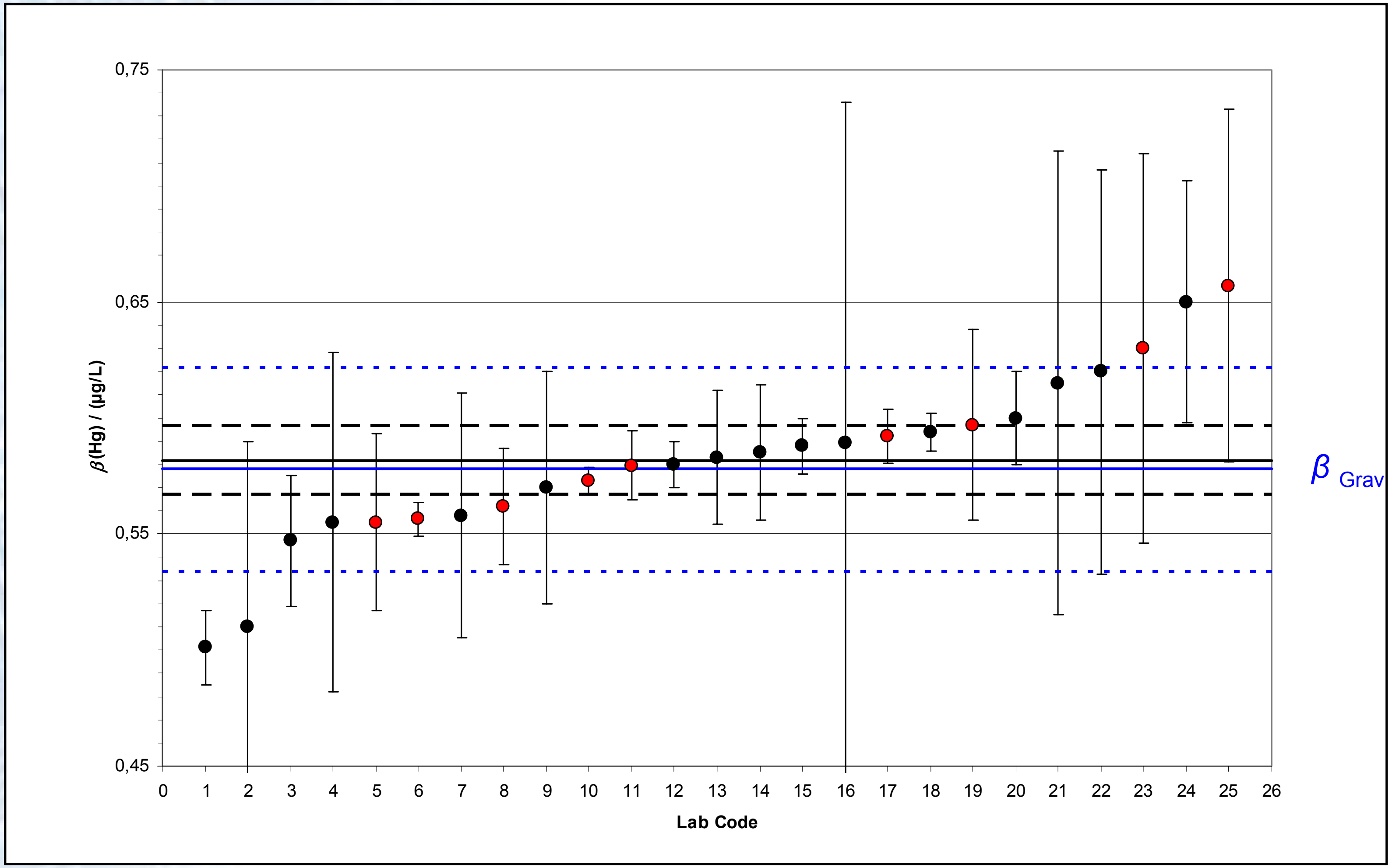


$\beta_{\text{Grav.}}$ = 0,578 ± 0,044 µg/l

$\beta_{\text{Arith. mean}}$ = 0,582 ± 0,014 µg/l

s_{rel} = 6,3%

Mercury (natural water samples)



$\beta_{\text{Grav.}}$ = 0,578 ± 0,044 µg/l

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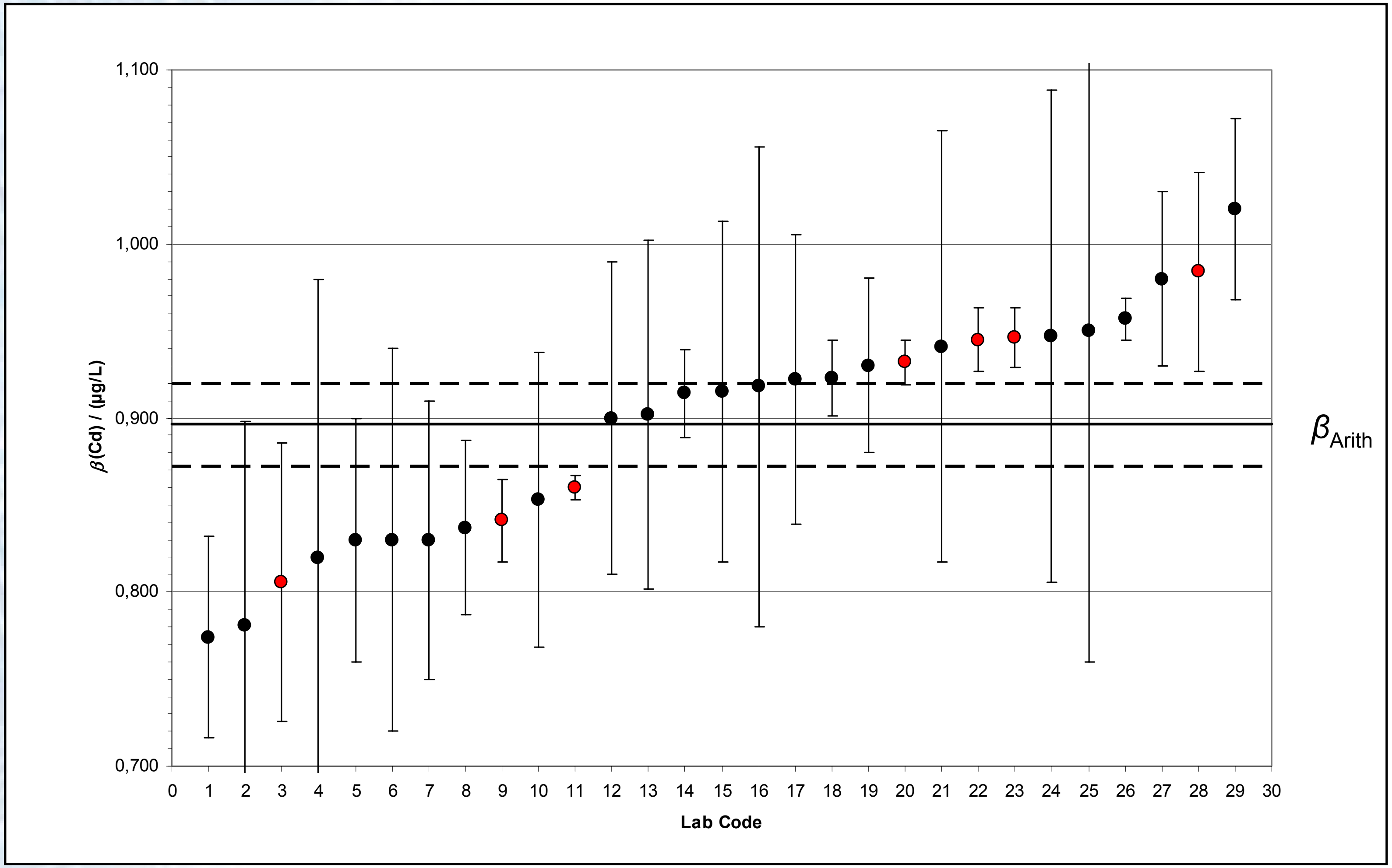
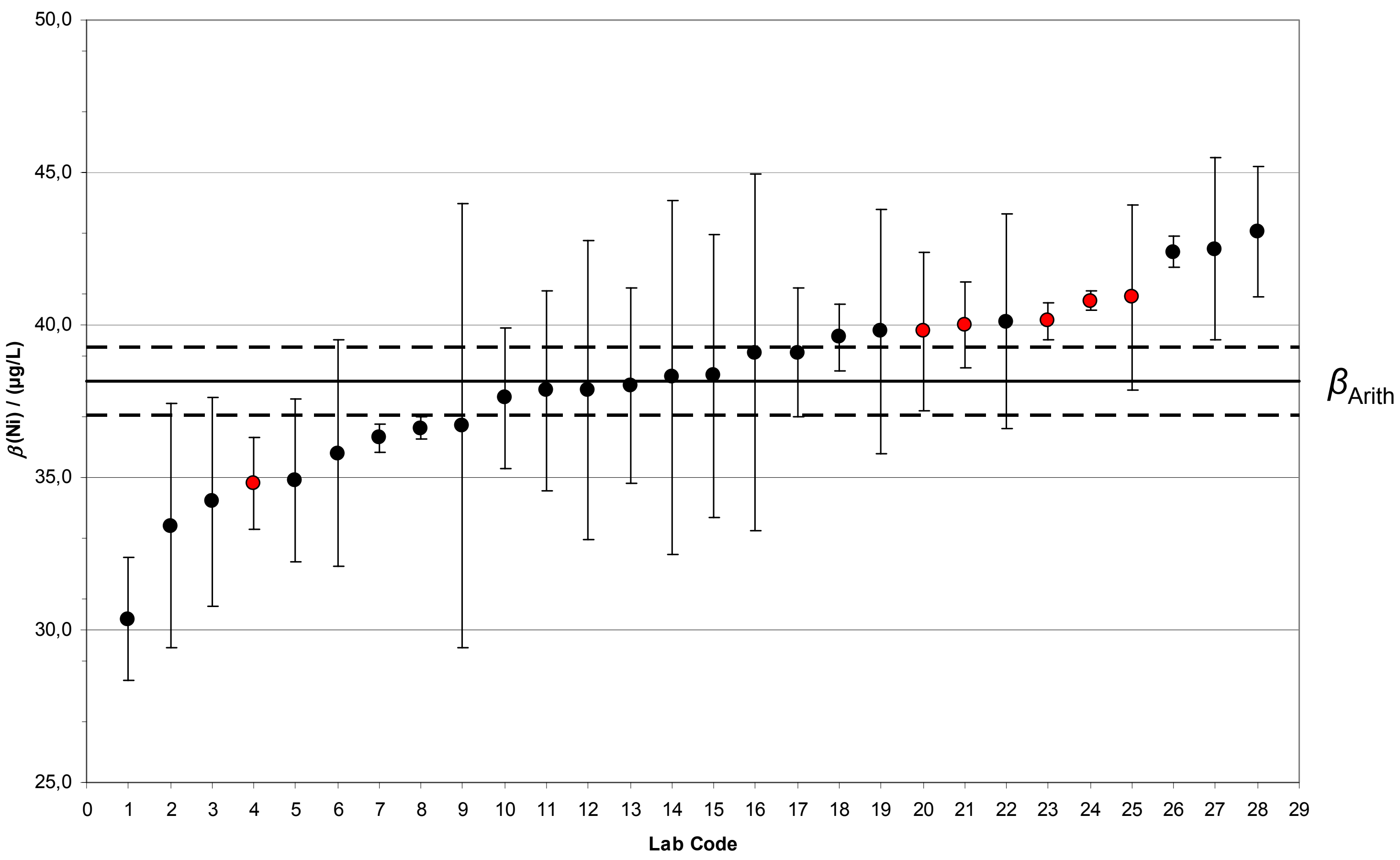
Cadmium (natural water samples)



$\beta_{\text{Arith. mean}}$ = 0,896 ± 0,025 µg/l

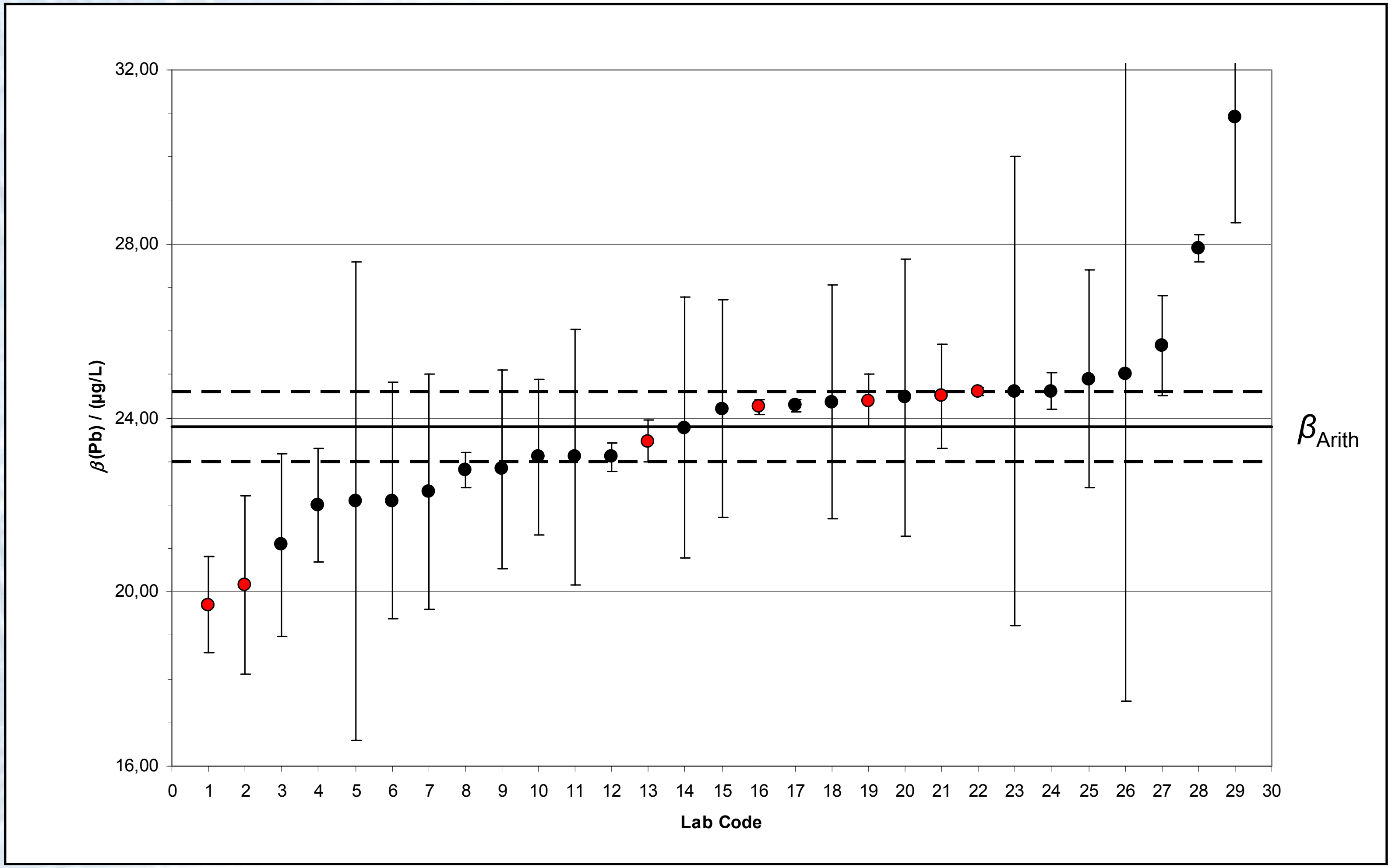
s_{rel} = 7,2%

Nickel (natural water samples)



$\beta_{\text{Arith. mean}}$ = 38,15 ± 1,17 µg/l
s_{rel} = 7,7%

Lead (natural water samples)



$\beta_{\text{Arith. mean}}$ = 23,83 ± 0,83 µg/l

s_{rel} = 9,1%

Measurement techniques for Hg

		β_m in µg/l	s in %
Pure water	ref.:	0,0470	4,8
4 AAS		0,0545	15,2
8 AFS		0,0485	5,9
4 ICPMS		0,0591	34,5
4 ID ICPMS		0,0498	5,8
Natural water	ref.:	0,578	7,8
AAS		0,597	6,9
7 AFS		0,575	4,8
5 ICPMS		0,550	8,1
5 ID-ICPMS		0,593	6,3

All instruments are used in combination with cold vapor technique

Influence factors

	Pure water		Natural water		Enhancement of concentration
	s in %	**$\Delta\beta$** in %	**s** in %	**$\Delta\beta$** in %	
Hg	7,9 (3)		6,3		10
Cd	6,9		7,2		5
Ni	4,9 (1)		7,7		2
Pb	4,3		9,1		3

( ) Outliers of PCLs

$$\Delta\beta = \beta_{grav} - \beta_{arth}$$

Influence factors

	Pure water		Natural water		Enhancement of concentration
	s in %	**$\Delta\beta$** in %	**s** in %	**$\Delta\beta$** in %	
Hg	7,9 (3)	-2,2 (3)	6,3	-0,67	10
Cd	6,9	1,1	7,2	-	5
Ni	4,9 (1)	-2,0 (1)	7,7	-	2
Pb	4,3	-1,1	9,1	-	3

( ) Outliers of PCLs

$$\Delta\beta = \beta_{grav} - \beta_{arth}$$

Comparison PCLs-NMIs

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	Pure water		Natural water	
	s in %	$\Delta\beta$ in %	*s* in %	$\Delta\beta$ in%
PCLs				
Hg	8,1 (3)		6,6	
Cd	7,7		7,3	
Ni	4,9 (1)		8,0	
Pb	4,5		8,9	
NMIs				
Hg	7,6		5,9	
Cd	3,5		7,3	
Ni	1,2 (1)		1,2 (1)	
Pb	1,3 (1)		1,9 (2)	

NMI-outliers: unexperienced or an inappropriate method was used

Comparison PCLs-NMIs

	Pure water		Natural water	
	s in %	**Δ*β*** in %	***s*** in %	**Δ*β*** in%
<u>PCLs</u>				
Hg	8,1 (3)	0,7 (3)	6,6	0
Cd	7,7	-1,6	7,3	-
Ni	4,9 (1)	-0,4 (1)	8,0	-
Pb	4,5	0,9	8,9	-
<u>NMIs</u>				
Hg	7,6	4,6	5,9	1,9
Cd	3,5	0,6	7,3	-
Ni	1,2 (1)	0,1 (1)	1,2 (1)	-
Pb	1,3 (1)	0,3 (1)	1,9 (2)	-

NMI-outliers: unexperienced or
an inappropriate method was used

SWIFT results

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µg L⁻¹	RM01				RM12			
	N° of participants	% outliers	Consensus value	CV %	N° of participan	% outliers	Consensus value	CV %
Al	21	48.0	3.6±0.5	12.6	41	14.6	45.8±8.0	17.5
As	31	16.0	1.2±0.3	22.9	26	46.2	0.63±0.18	28.6
Cd	28	29.0	0.03±0.02	53	27	14.8	0.07±0.05	71.8
Cr	23	17.0	0.42±0.2	48.6	36	50.0	0.57±0.26	45.6
Cu	41	15.0	2.7±0.6	20.5	42	31.0	3.37±0.6	17.8
Mn	34	15.0	54. 8±5.1	9.3	47	6.4	154±17	11.0
Ni	39	8.0	4.4±0.9	21.6	32	37.5	1.10±0.43	39.1
Pb	28	36.0	0.2±0.08	37.5	31	38.7	0.68±0.25	36.8
Se	12	17.0	0.52±0.4	73.1	14	21.4	1.61±1.41	87.6
Zn	40	15.0	14.9±1.5	9.7	39	12.8	12.2±2.5	20.5

µg L⁻¹	RM03				RM05			
	N° of participants	% outliers	Consensus value	CV %	N° of participants	% outliers	Consensus value	CV %
Al	27	4.0	152±20	13.1	49	20.4	42.9±6.0	14
As	38	8.0	7.2±0.8	10.5	59	7.1	10.1±1.2	12
Cd	46	20.0	6.5±0.8	12.7	62	8.1	5.7±0.6	10.1
Cr	34	15.0	62.1±5.4	8.7	60	16.7	4.1±0.6	15
Cu	45	22.0	1255±47	3.7	66	6.2	78.8±5.9	7.5
Mn	32	6.0	69.1±6.6	9.6	63	3.2	58.0±4.6	7.9
Ni	46	9.0	22.3±2.5	11.1	60	1.8	7.3±1.2	17.1
Pb	44	30.0	12.7±1.5	12.2	59	7.0	10.6±1.7	16.3
Se	18	11.0	8.28±1.3	16.1	64	0.0	10.0±3.4	33.9
Zn	45	9.0	142±11	7.5	43	11.5	45.2±3.9	8.6

Table VIII: Summary of results for the SWIFT-WFD PTs exercises on trace elements determination.

Measurement capability of the PCLs

	Swift RM03			Euramet 924, part 2		
	c in µg/l	s in%	z_{mean}	c in µg/l	s in %	z_{mean}
Cd	5,7	11 (8)	1,5	0,9	7,3	0,9
Ni	22	14 (9)	1,0	37,8	8,0	0,8
Pb	13	15 (30)	3,8	23,8	8,9	0,7

( ) outliers in %

$z = \text{abs}((x - x_{mean})/s)$

Measurement capability of PCLs seems to be sufficient for taking over a task in the dissemination chain

Further Activities

PTB

- Poster presentation at „Water Status Monitoring under the WFD Conference“ in Lille, 12.-14. March 2007
- Presentation of the project at the „Chemical Monitoring Activity“ meeting in Berlin, 2. May 2007 (invitation of Philippe Quevauviller)
- Organisation of CCQM-P100.1/2 parallel to Euramet 924

Time schedule

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Step 1	**“Link of the NMIs an PCLs”** Euramet 924 part 1 (CCQM-P100.1) Euramet 924 part 2 (CCQM-P100.2) Draft report A for CCQM	April 2007
Step 2	**“Validation of the measurement procedures”** Meeting in the PTB including a Workshop on uncertainty estimation	April 2008
Step 3	**“Link of the PCLs and test laboratories”** Comparison presumabliy by the end of 2008 Parallel CCQM key comparison for Hg	by 2009

Next comparison

PTB

Subject:	Hg in natural water		
Analyte:	Hg on EQS concentration level (about 0,050 µg/L)		
Preparation:	Rheinisch-Westfälisches Institut für Wasserwirtschaft (IWW)		
Organisation:	PTB, BAM, LNE, IRMM		
	Parallel to the Euramet 924 comparison for test laboratories + PCLs + NMIs		
Timeschedule:	Registration	summer	2008
	Sample dispatch	by the end of	2008
	Submission of the results	by April	2009

Thanks for your attention