NORMAN Interlaboratory study (ILS) on passive sampling of emerging pollutants

STUDY RESULTS: challenging substances – Steroid hormones, PFOS/PFOA, Bisphenol A, Triclosan

Chemical Monitoring On Site (CM Onsite) organised by NORMAN Association and JRC in support of CIS WFD

Cécile Miège

Irstea, freshwater systems, ecology and pollution research unit, Lyon, France

Design of the exercise

Steroid hormones*: *15 laboratories
17-alpha-Estradiol (17 αE2)
17-alpha-Ethinylestradiol (17 **α**EE2)
17-beta-Estradiol (17 **β**E2)
Estriol (E3)
Estrone (E1)
➔ Cemagref (Irstea) as ref. lab.

Bisphenol A (BPA): 11 laboratories
➔UK Environment Agency as ref. lab.

Triclosan (TCL): 8 laboratories
➔UK Environment Agency as ref. lab.

Fluorinated surfactants : 9 laboratories
PFOA, PFOS
➔European Commission
DG Joint Research Centre as ref. lab.

➲ Campaigns on site : in June-July 2011

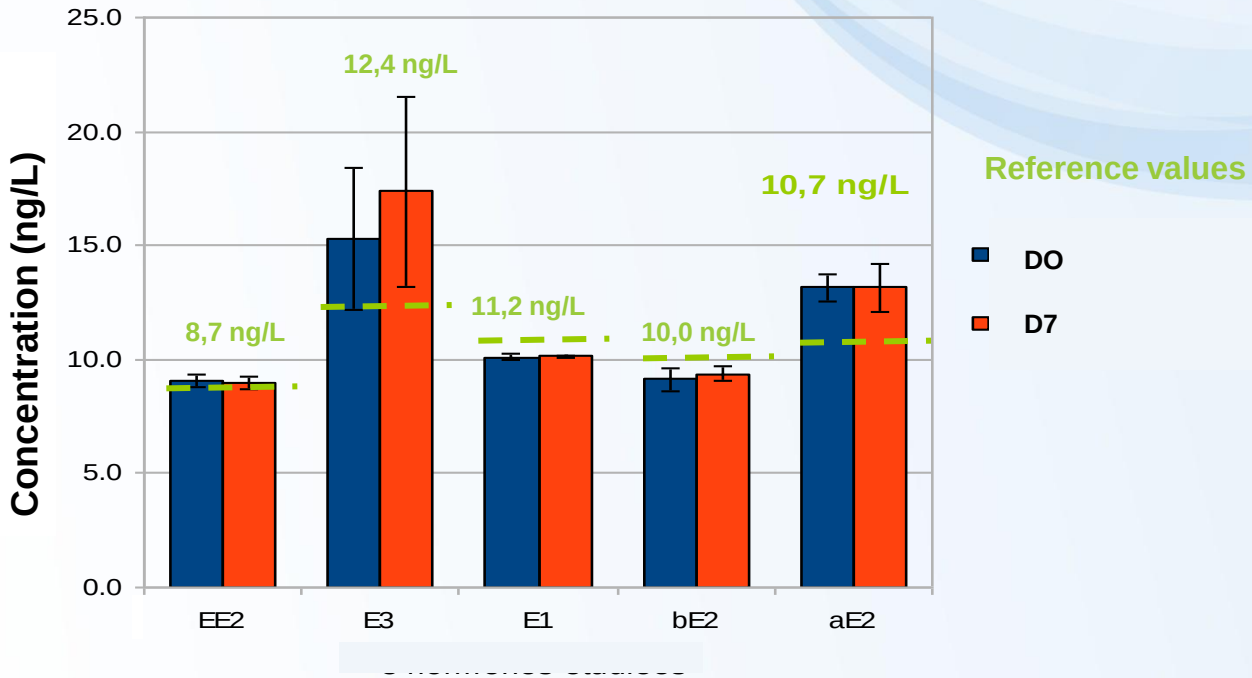
Preliminary study on stability for steroids (1)

Unstability of steroids in water (4 C, white glass containers)

- α EE2 not degraded after 72h
- αE2 et βE2 degraded → E1

Preliminary study on stability for steroids (2)

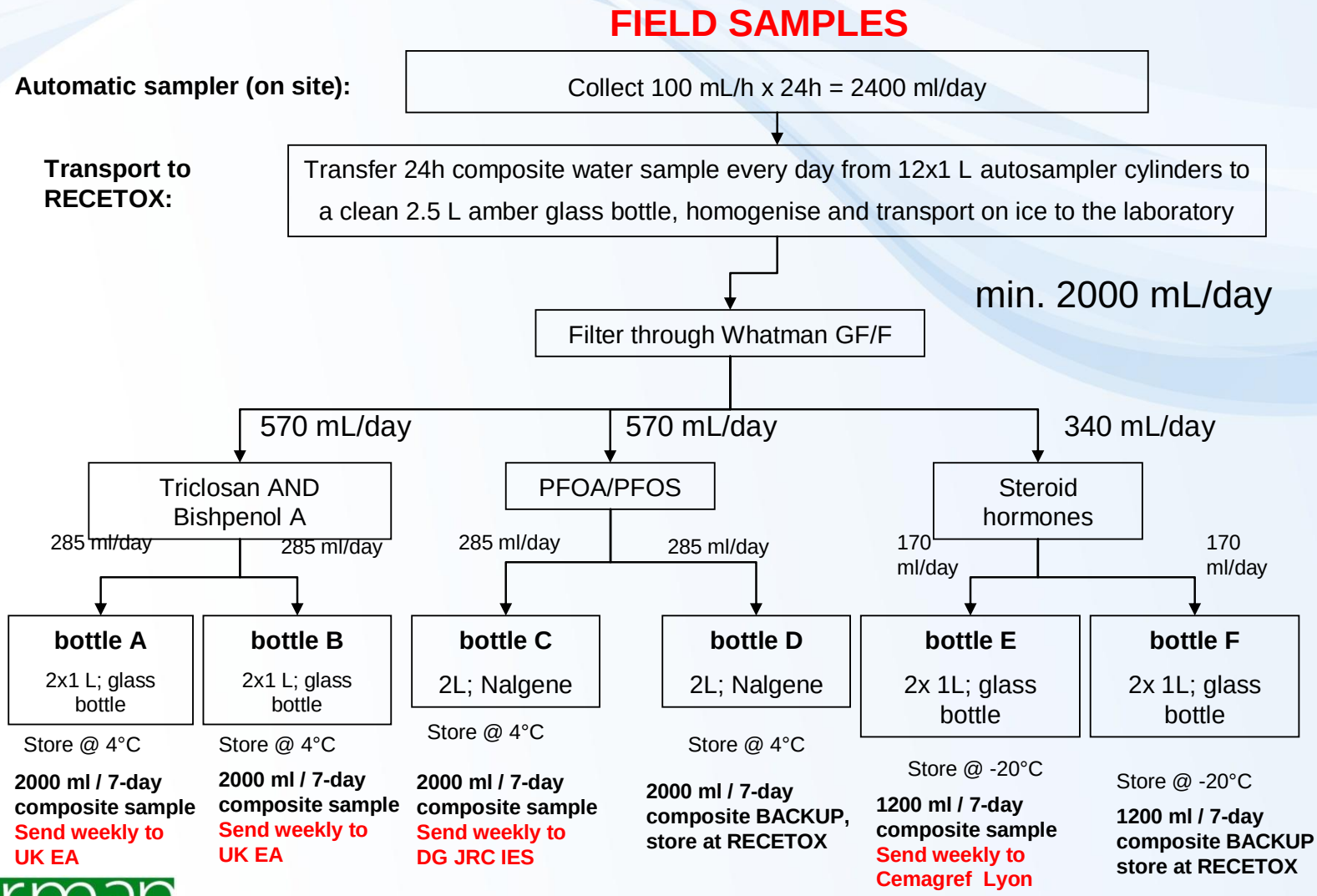
- Spiking level ~10 ng/L
- Matrix : wastewater treatment plant effluent
- Storage in amber glass containers at -20°C during 7 days
- Defrosting at 4°C



➲ **Stability of steroids when waters are frozen and stored in amber glass containers and defrosted at 4 C**

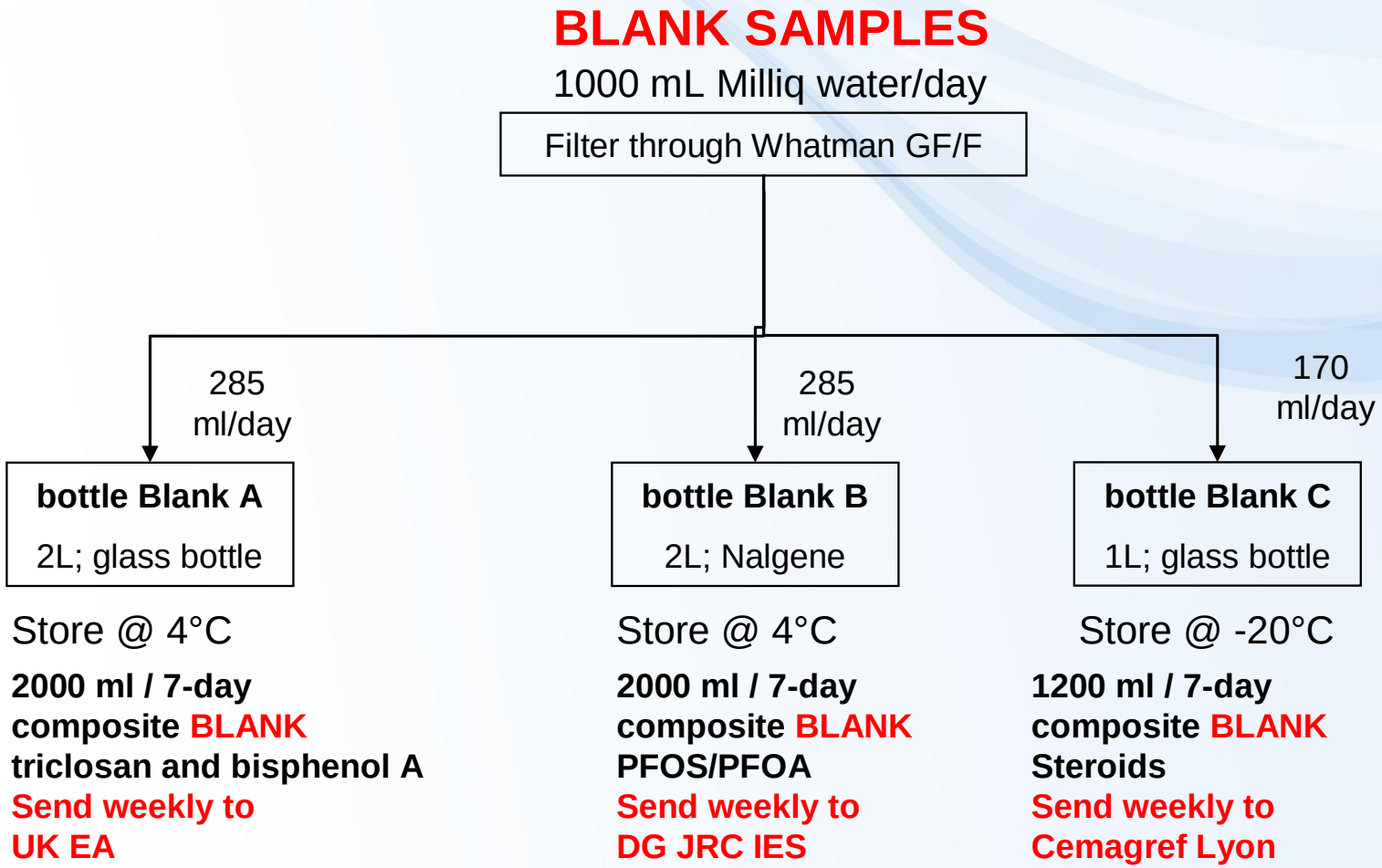
WATER SAMPLING PROTOCOL- field samples

Steroid hormones, PFOS/PFOA, Bishpenol A, Triclosan



WATER SAMPLING PROTOCOL- blank samples

Steroid hormones, PFOS/PFOA, Bishpenol A, Triclosan



Self assessed level of expertise in analysis of target compound groups in passive samplers

Laboratory	Steroid hormones	Fluorinated surfactants	Triclosan	Bisphenol A
16	A	A	C	A
19	B	B	B	B
20	C		B	C
21		C		
23	B	A	A	A
26	C			C
29		A		
31	A			
33	A			
36	B			
37	C	C		
39	B	B		B
43	B			
44	C	C	C	C
45	B			B
47			B	B
49	A		A	B
50	C		C	C
52		A		

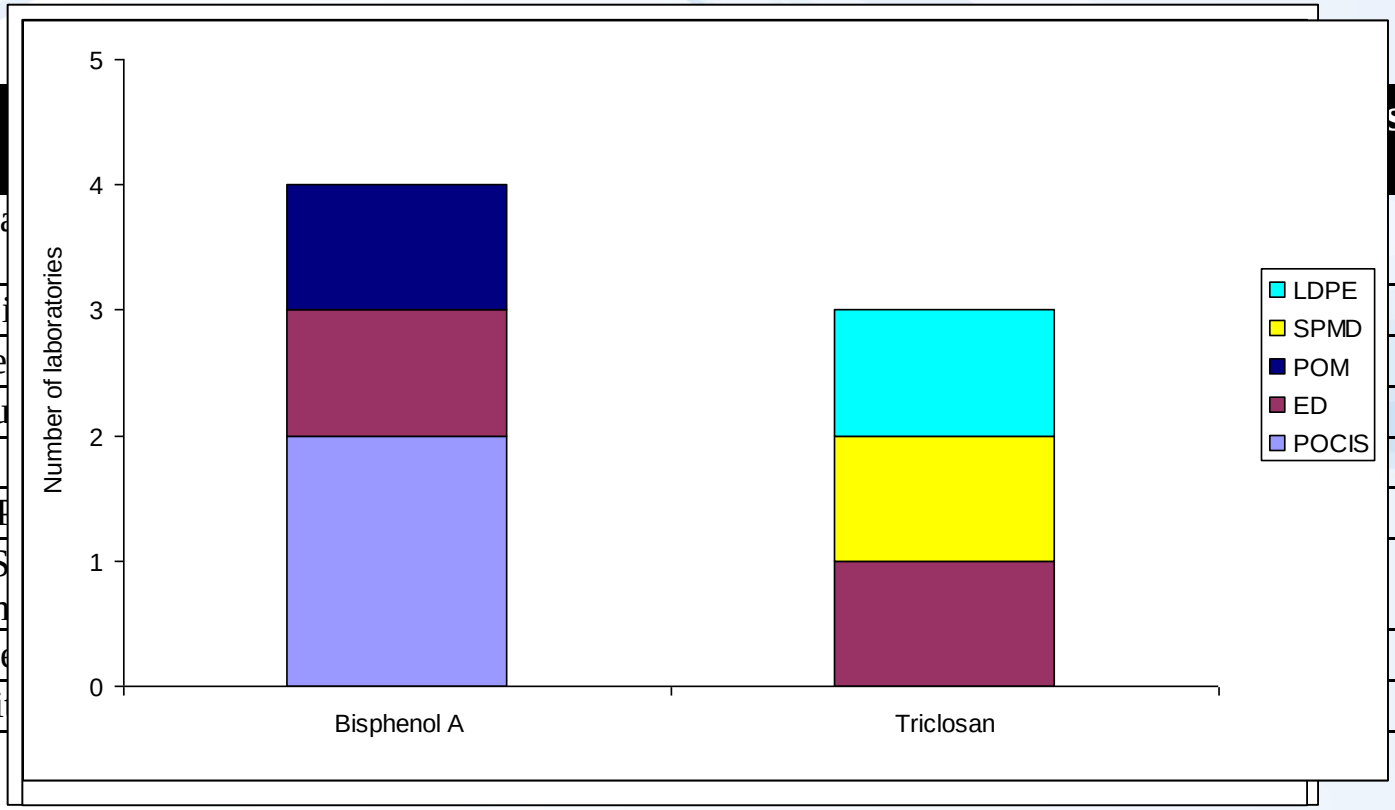
A- expert

B-some experience

C-limited experience

Categories of participant samplers

Sampler	sphenol
POCIS pha version	39, 45
Empore Di	
POCIS, pe	
Silicone ru	
Speedisks	
Modified F	
Standard S (length 1m	
Polyoxyme	
Low densi	



Results for steroid hormones

Example :
17 beta Estradiol

•**QC** : the median and geometric mean of participant within the uncertainty range stated by the central laboratory

	Stand. Solution µg/mL
Median	0.0204
s	0.011
Geomean	0.022
n	13
Outliers	2
s excl. outl	0.0050
Refvalue	0.02
Exp. Unc	0.00

	Provided Sampler uptake ng/cm2
Median	0.035
s	0.099
Geomean	0.060
n	6
Outliers	0

Log_2 scale

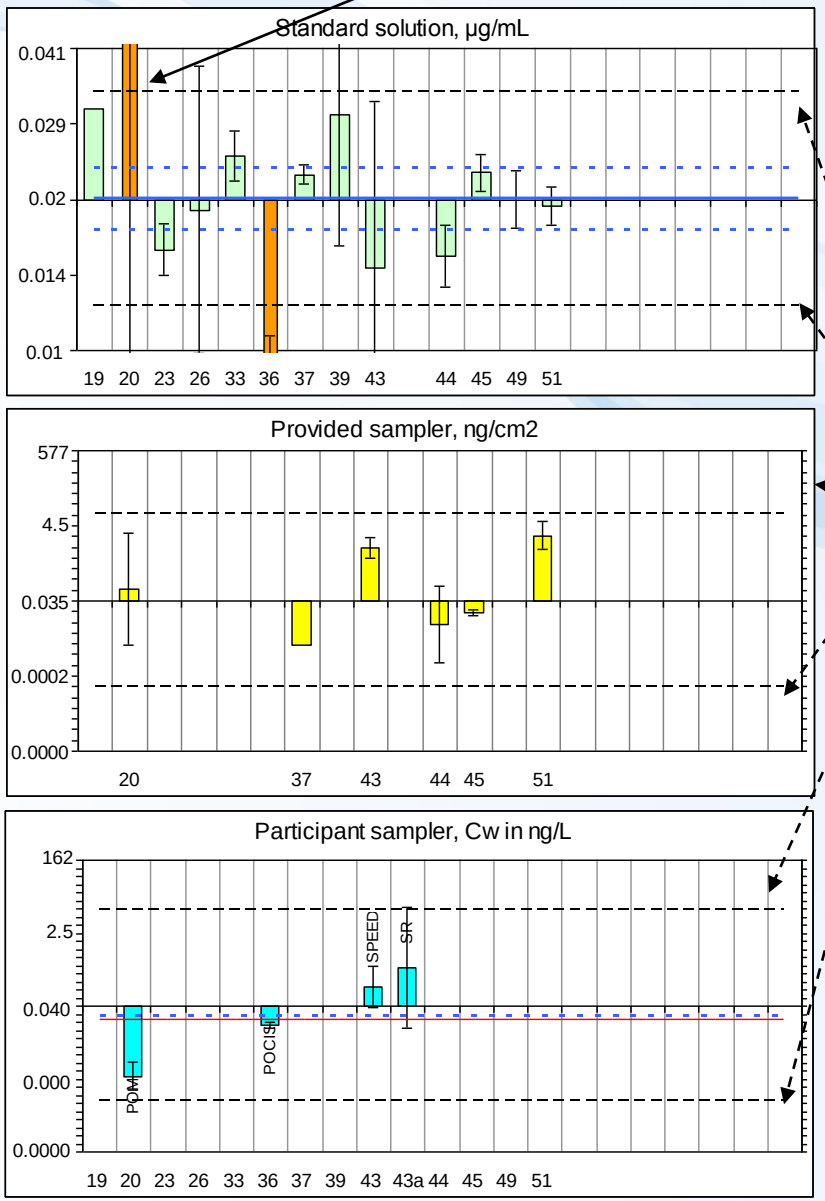
•Only 4 lab for participant sampler (in ng/L)

☛ TWAC< LOQ

	Participant Sampler Cw ng/L
Median	1.33
s	5.4
GeomMean	0.66
n	4
Outliers	0

Spot samples	
Period 1	0.54
Period 2	0.58
LOD	

outliers



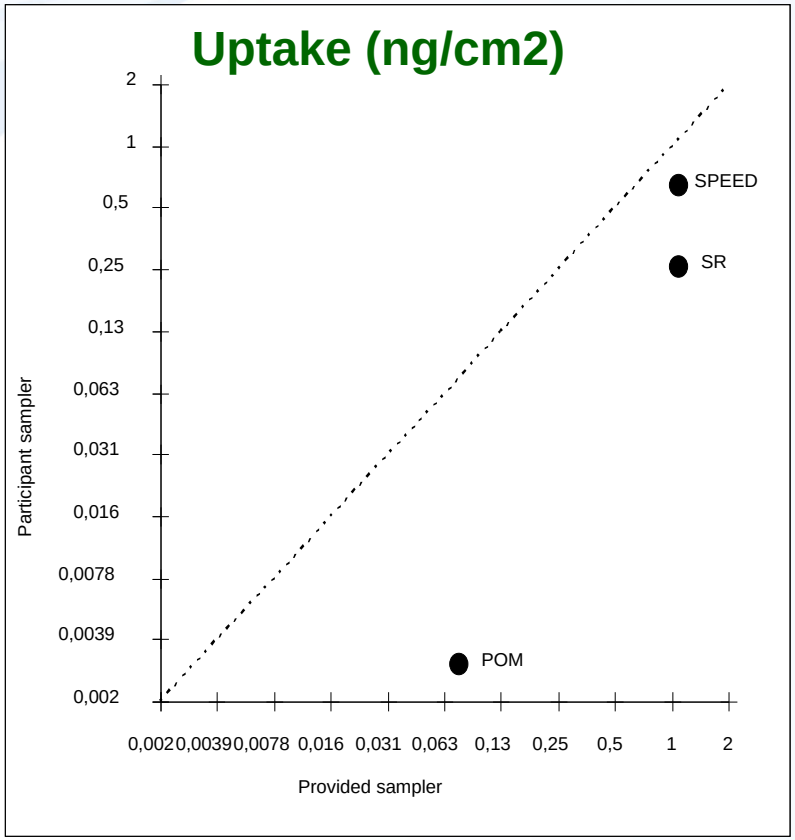
Set value expanded Uncertainty (k = 2)

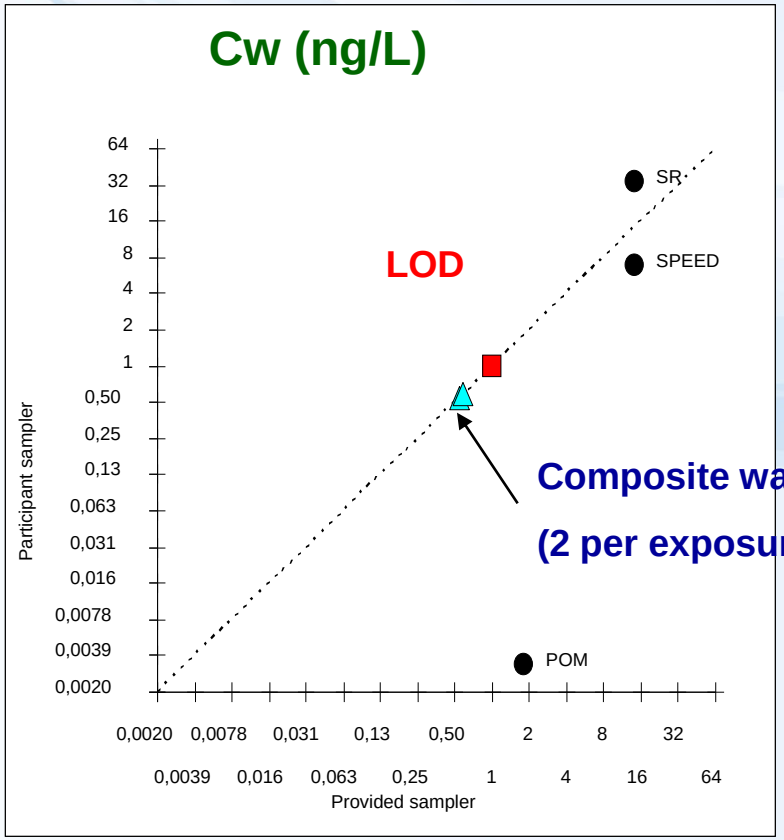
2 SD of log_2 transformed data

water sample mean

Laboratory number

Example 17 beta Estradiol – Samplers comparison

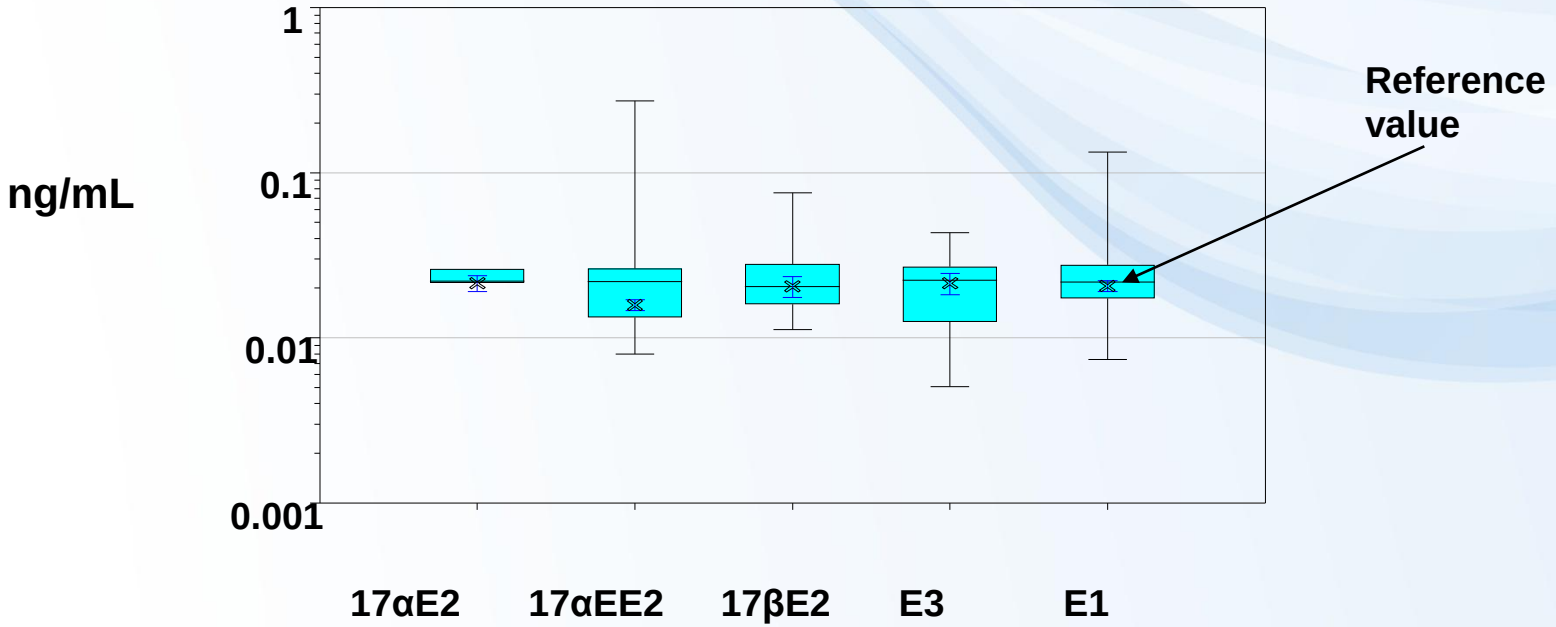




Standard solution

➲ 4 replicates of sample injection to the instrumental system

➲ Injections spread over the analysis sequences (at least 4 other sample injections are made between individual injections of this solution)



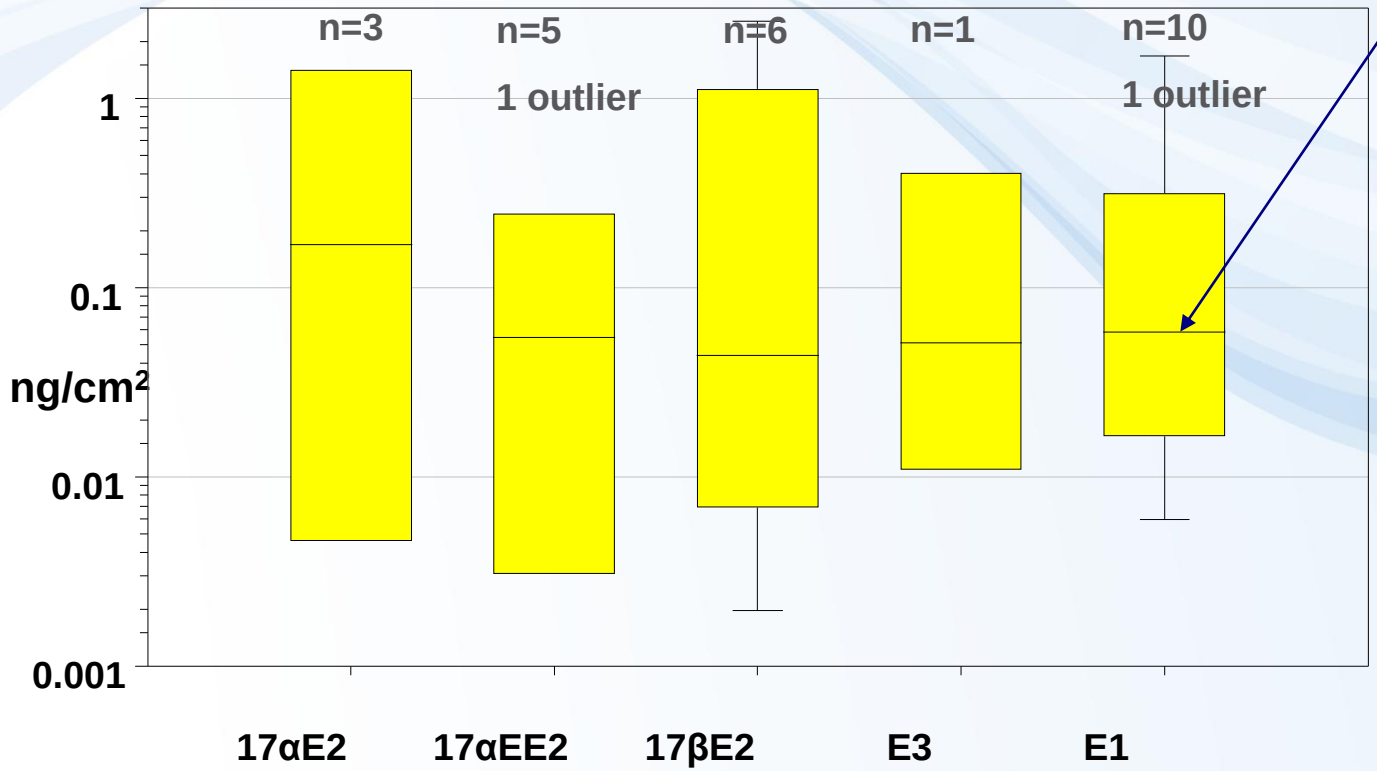
•Reference concentration of steroids within the range comprised by the participant results (median 2 standard deviations excluding outliers)

•Except for 17-αEE2, the median and geometric mean of participant results were within the uncertainty range stated by the central laboratory.

•Outlier results were reported by 3 laboratories (20, 23 and 36).

Provided sampler (= POCIS pharm without PRC)

➲ Analysis of triplicates of POCIS exposed for 14 d



Median value expanded uncertainty (k = 2)

Conc. in field blank close to LOD (< 10% Conc. in exposed samplers)

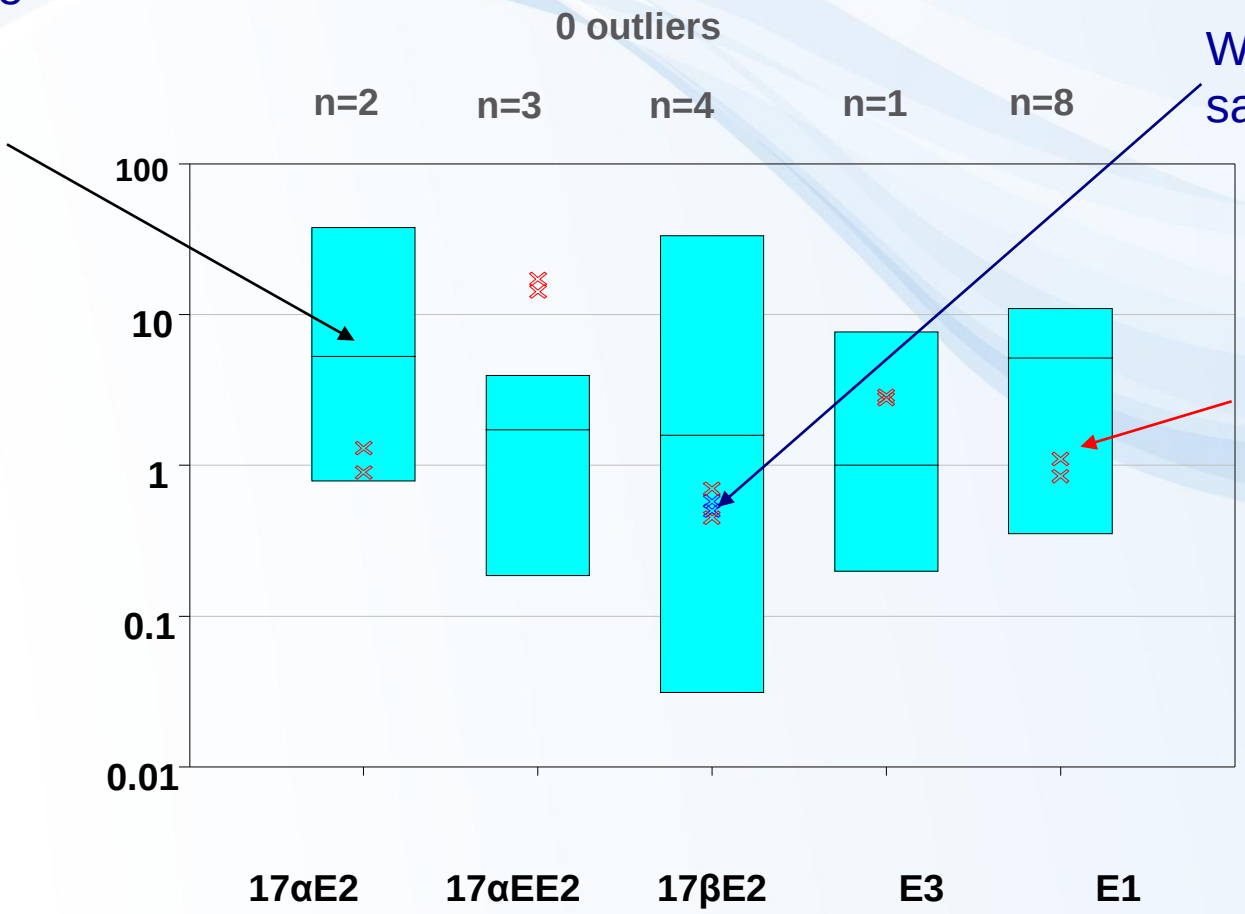
➲ Because of very low water concentration (see table right), < 6 lab. were able to measure steroids (except estrone) above their LOQs in provided samplers

Water concentrations

Sample/Compound	(bottle C1)[1] (20.6.-26.6.)	(bottle C2)[1] (27.6.-4.7.)	(bottle E1)[3] (20.6.-26.6.)	(bottle E2)[4] (27.6.-4.7.)	units
17-alpha-Estradiol	<1.30	<0.90	<1.05	<0.90	ng/L
17-alpha-Ethinylestradiol	<17.25	<14.2	<10.00	<11.98	ng/L
17-beta-Estradiol	0.70	<0.45	0.50	0.58	ng/L
Estriol	<2.90	<2.75	<7.45	<8.33	ng/L
Estrone	<1.10	<0.85	<0.85	<0.73	ng/L

Participant sampler, Cw

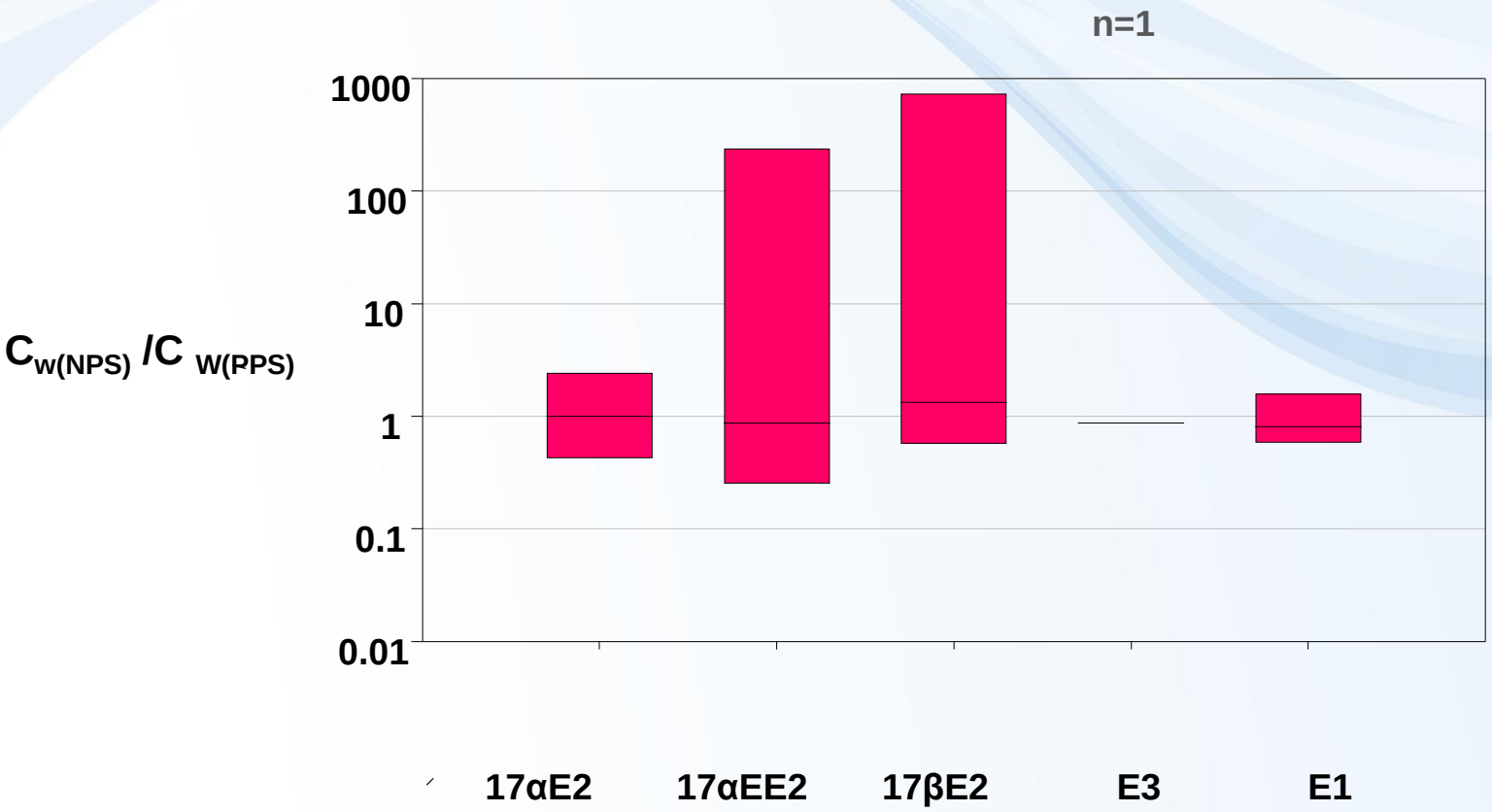
Median value expanded uncertainty (k = 2)



Weekly spot samples

LOD in spot samples

Ratio of water concentrations provided / participant sampler



NPS – provided passive sampler; PPS – participant passive sampler

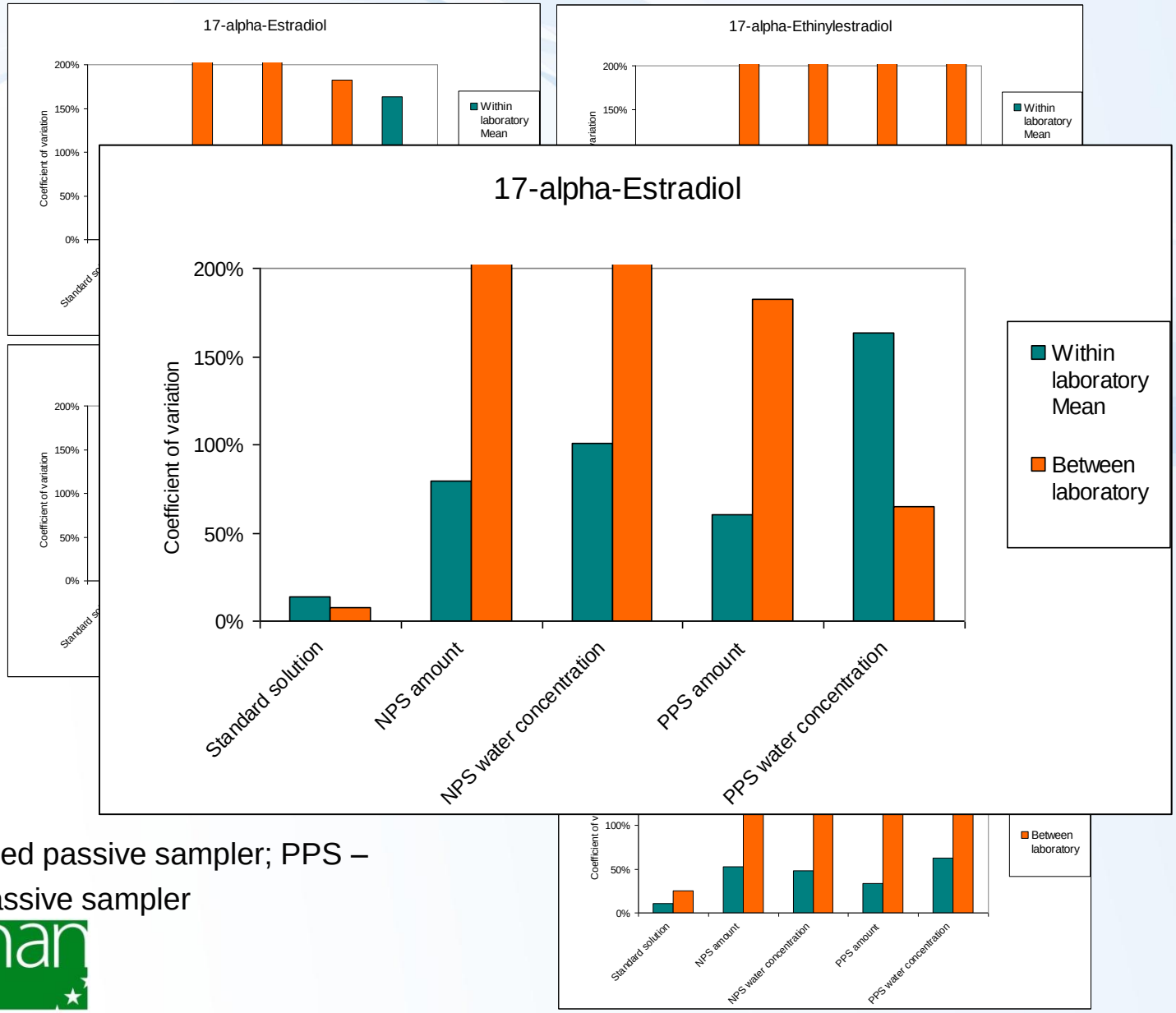
Variability of reported results (excluding outliers)

Steroid hormones					
		Coefficient of variation (%)			
Variability:		Within laboratory		Between laboratory	
Matrix analysed:		Min.	Max.	Min.	Max.
	Standard solution	11%	22%	8%	53%
Provided sampler	NPS amount	53%	>300%	208%	>300%
	NPS water concentration	48%	101%	251%	>300%
Participant sampler	PPS amount	3%	60%	154%	>300%
	PPS water concentration	3%	163%	65%	>300%

NPS – provided passive sampler; PPS – participant passive sampler

- High variabilities because concentrations in passive samplers close to LOQs
- Analysis of steroids in complex environmental matrixes is challenging

Variability of reported results



NPS – provided passive sampler; PPS – participant passive sampler

Conclusions for steroids

- Standard solution :
  - ➲ acceptable variability with exception of 17-α-EE2 (between lab. variability of 53%)
  - ➲instrumental methods was not expected to cause excessive variability in reported data

- Analysis of steroids in passive samplers = a challenge
  - ➲ high within laboratory variability explained by concentrations close to LOQs + matrix effect + non-homogeneity of sampling

- A direct comparison of passive sampling data with spot sampling not possible since spot sample data below LOQ.

  However, no contradiction between passive sampling and spot sampling results

- Passive sampling method allows measurement of concentrations lower than spot sampling but the interlaboratory precision is not sufficient

Results for PFOS and PFOA

+ 2 × stand. dev. of log_2 transf. data
median
- 2 × stand. dev. of log_2 transf. data
+ expanded uncertainty with $k = 2$
reference value
- expanded uncertainty with $k = 2$

SPMD
sampler type
repeatability (± 2 × SD)
mean value
outlier colour

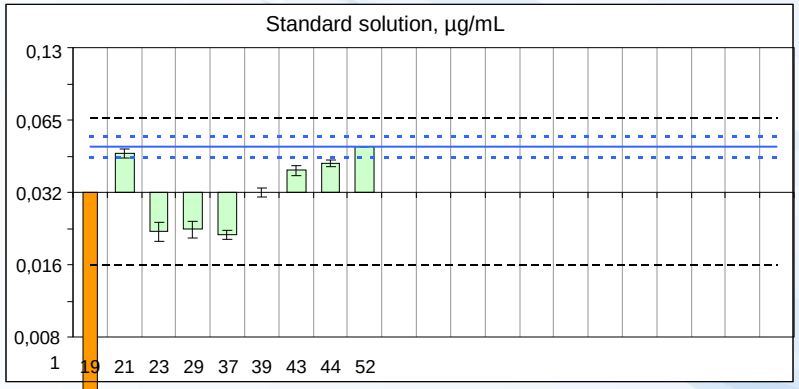
composite water sample (2 per exposure)
water sample mean

Example :

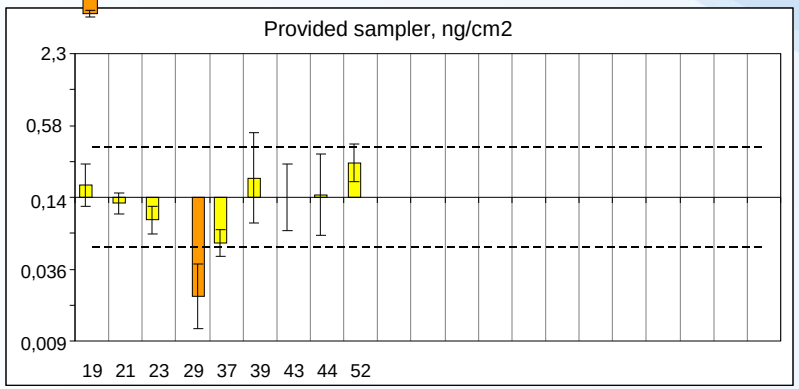
PFOS

•**QC :** the median and geometric mean of participant not within the uncertainty range stated by the central laboratory (not for PFOA)

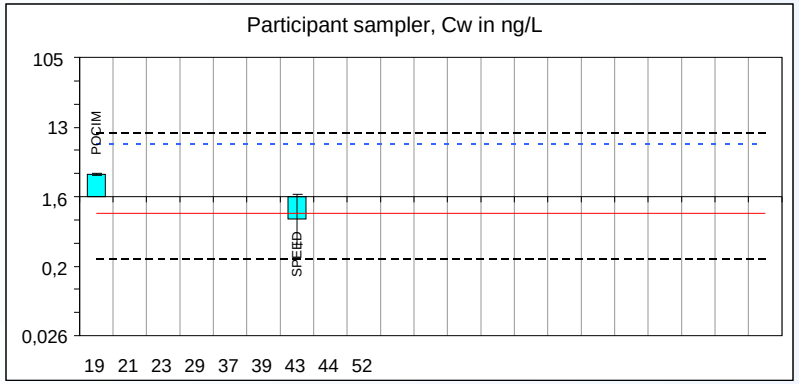
* Only 2 lab for participant sampler (in ng/L) ☛ passive sampler calibration is scarce (no calibration data available)



Stand. Solution µg/mL	
Median	0.032
s	0.024
Geomean	0.026
n	9
Outliers	1
s excl. outl	0.011
Refvalue	0.05
Exp. Unc	0.01

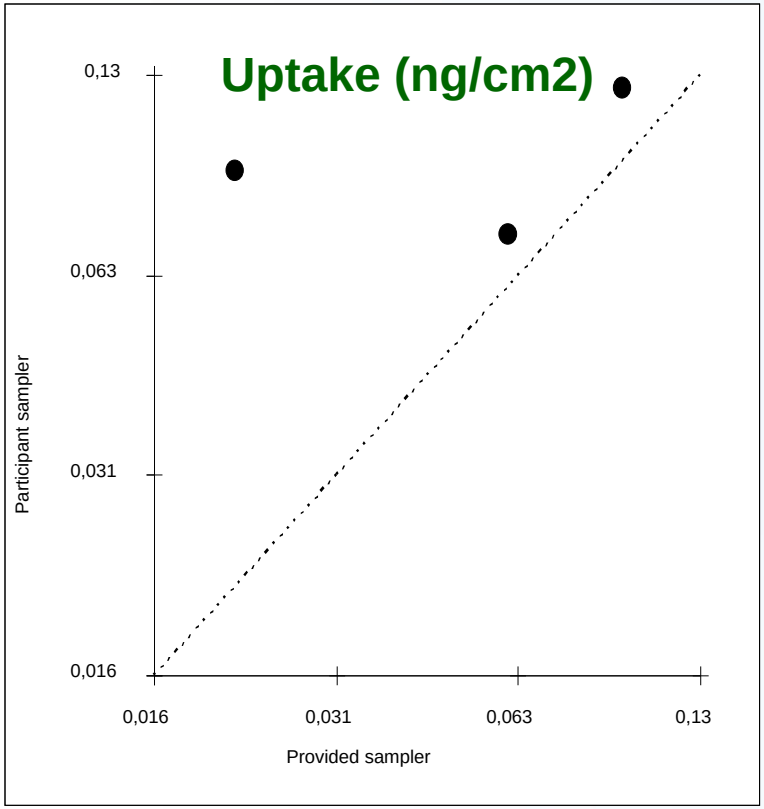


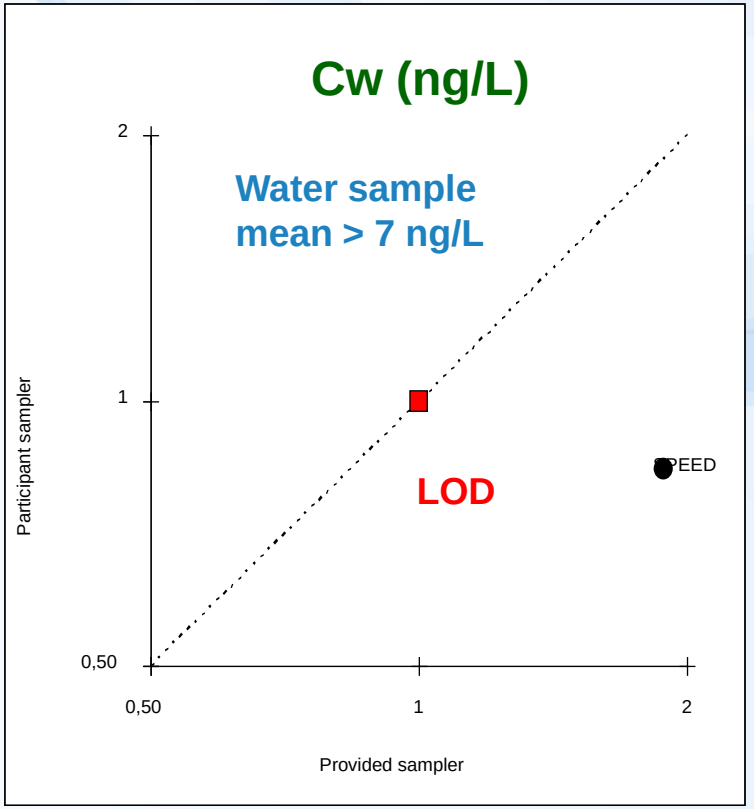
Provided Sampler uptake ng/cm2	
Median	0.144
s	0.112
Geomean	0.115
n	9
Outliers	1
s excl. outl	0.069



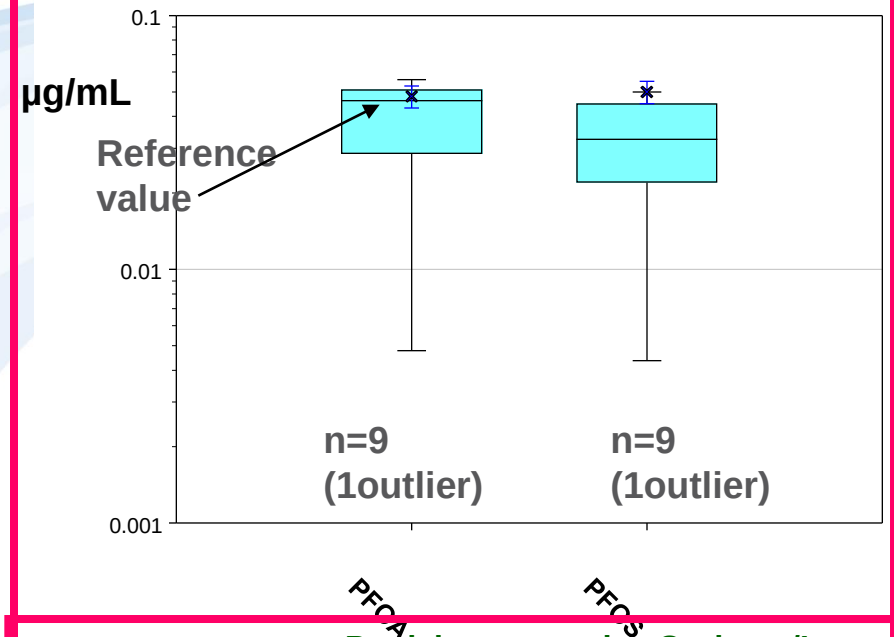
Participant Sampler Cw ng/L	
Median	1.64
s	1.6
GeomMean	1.6
n	2
Outliers	0
Spot samples	
Period 1	7.1
Period 2	8.5
LOD	1.00

Example PFOS - Samplers comparison

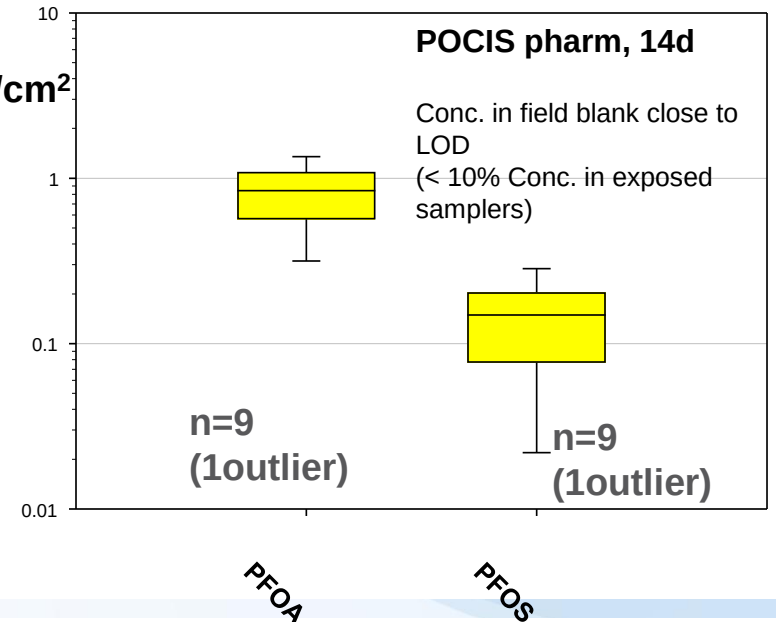




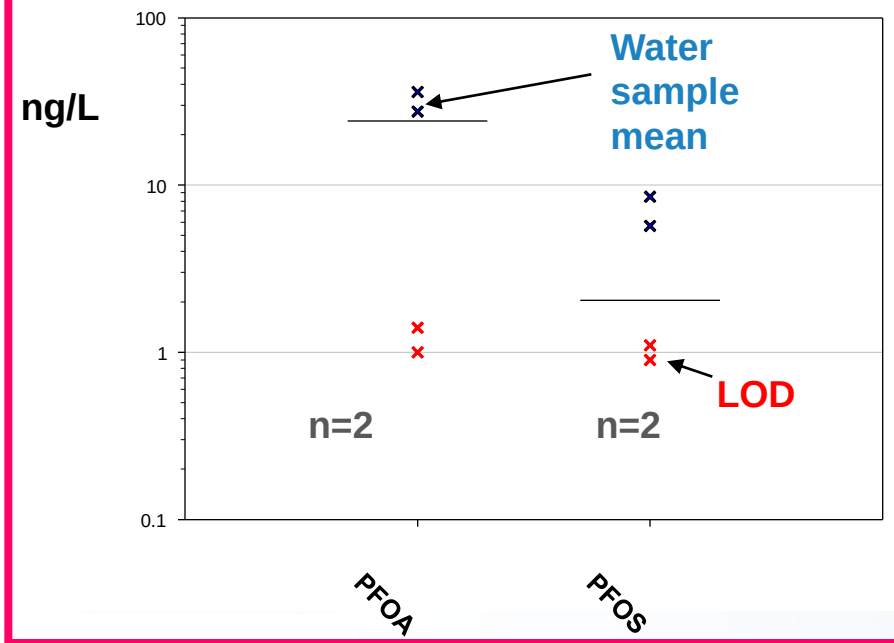
Standard solution, µg/mL



Provided sampler, ng/cm²



Participant sampler, Cw in ng/L



Sample/Compound	Bottle C1 (20.6.-26.6.)	Bottle C2 (27.6.-4.7.)	units
PFOA	27.5	36.0	ng/L
PFOS	5.7	8.5	ng/L

Variability of reported results

Fluorinated surfactants					
		Coefficient of variation (%)			
		Within laboratory		Between laboratory	
Variability:					
Matrix analysed:		Min.	Max.	Min.	Max.
Provided sampler	Standard solution	2%	2%	28%	37%
	NPS amount	15%	25%	36%	51%
	NPS water concentration	5%	9%	n.d.	n.d.
Participant sampler	PPS amount	18%	25%	64%	67%
	PPS water concentration	20%	21%	n.d.	n.d.

nd : because n=2 lab.

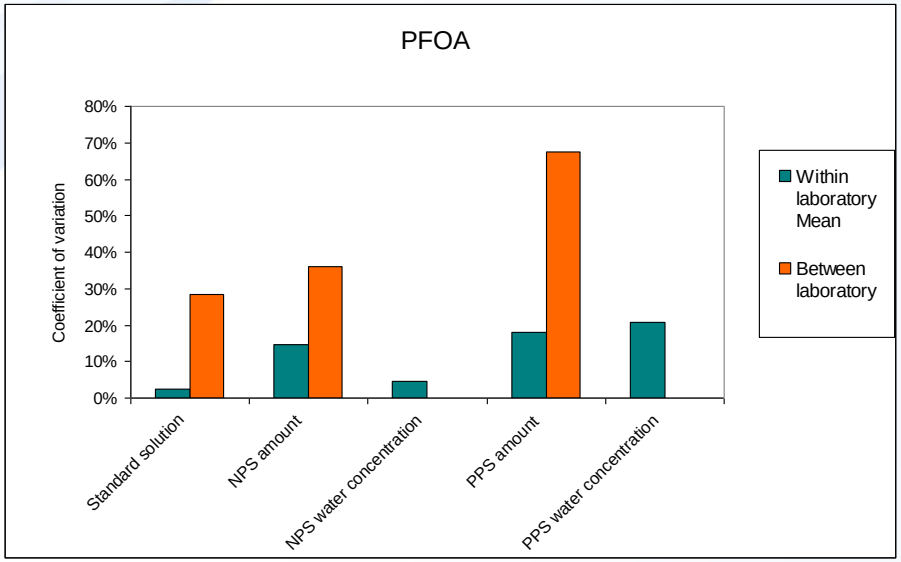
NPS – provided passive sampler; PPS – participant passive sampler

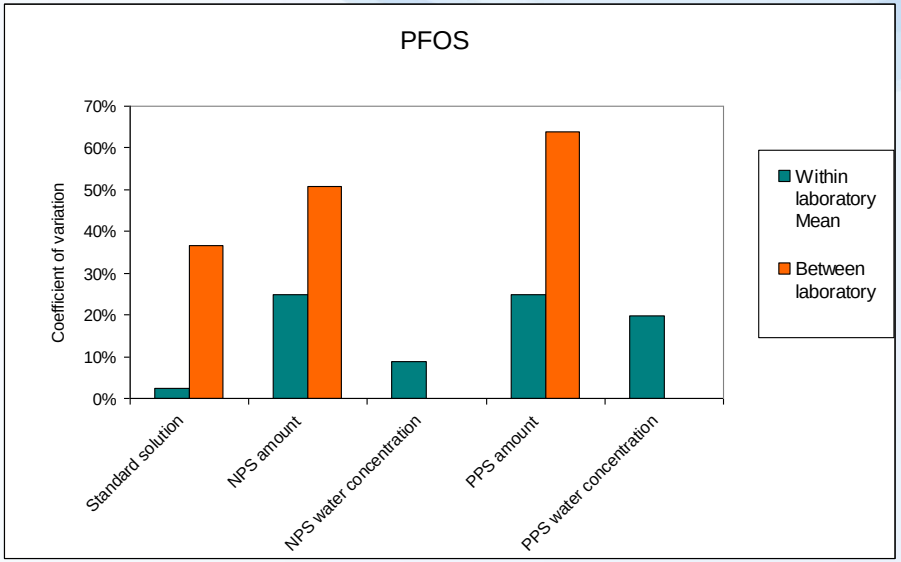
➲ **An excellent within laboratory variability of analysis of individual compounds in standard solution (2%)**

➲ **In provided samplers for sampler uptake : a good within laboratory variability (15 to 25%) and acceptable between variability (<51%)**

➲ **In all samplers : no possible to evaluate a between laboratory variability for water concentration (n=2)**

Variability of reported results





Results for BPA and TCL

+ 2 × stand. dev. of log_2 transf. data
median
- 2 × stand. dev. of log_2 transf. data
+ expanded uncertainty with $k = 2$
reference value
- expanded uncertainty with $k = 2$

SPMD ← sampler type
← repeatability (± 2 × SD)
← mean value
← outlier colour

composite water sample (2 per exposure)
water sample mean

Example :

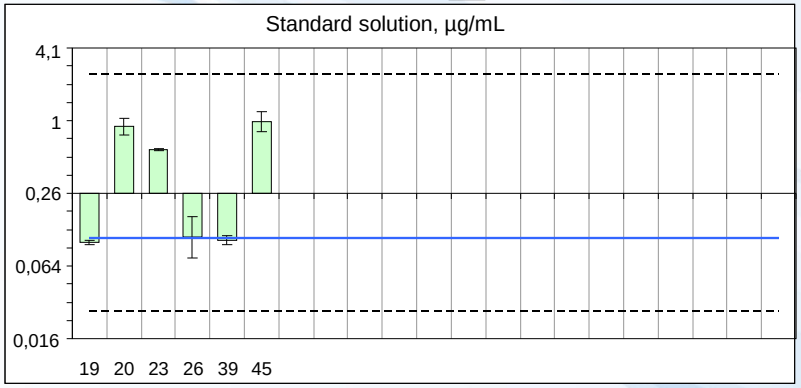
BPA

* **QC** : the median and geometric mean of participant > reference value (idem for TCL)

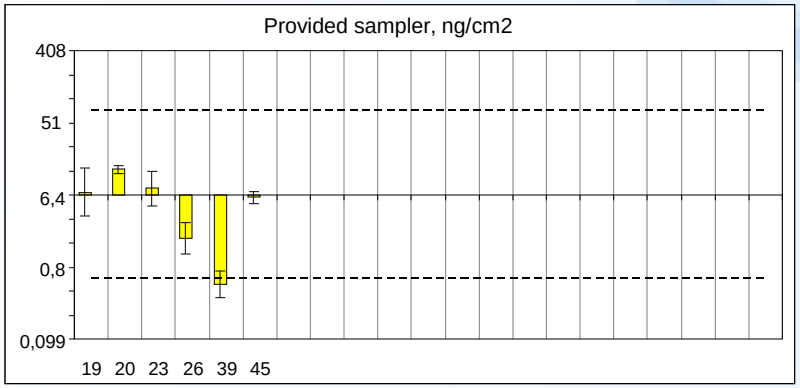
•Participant sampler (in ng/L) :

☛ Only 3 lab, because calibration is scarce (no calibration data available)

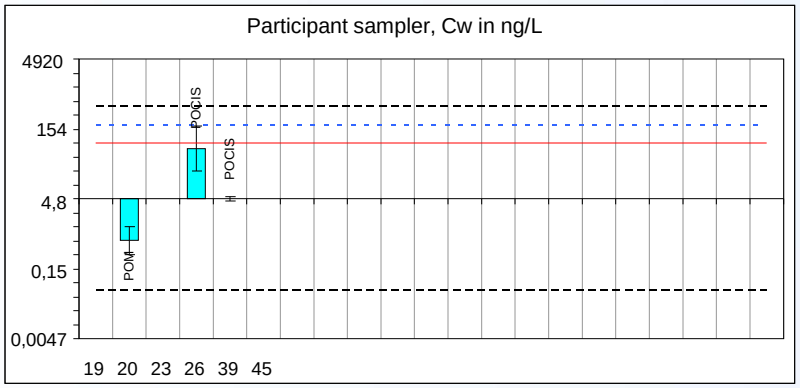
☛ median value < LOD < water sample mean



	Stand. Solution µg/mL
Median	0.258
s	0.29
Geomean	0.29
n	6
Outliers	0
Refvalue	0.11
Exp. Unc	0.00



	Provided Sampler uptake ng/cm2
Median	6.4
s	7.7
Geomean	3.9
n	6
Outliers	0

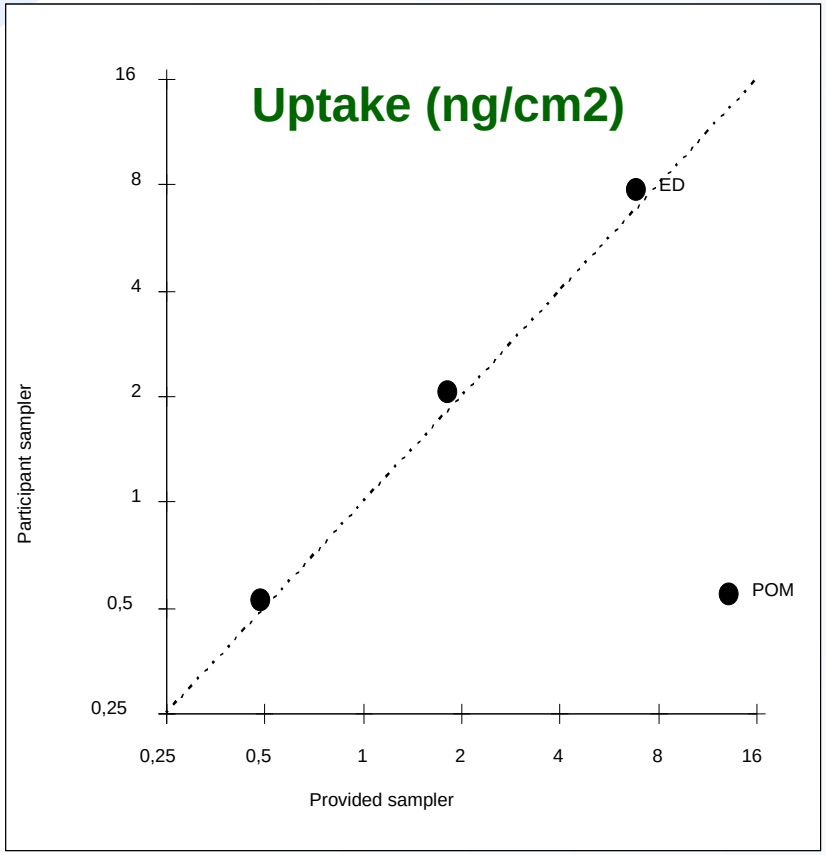


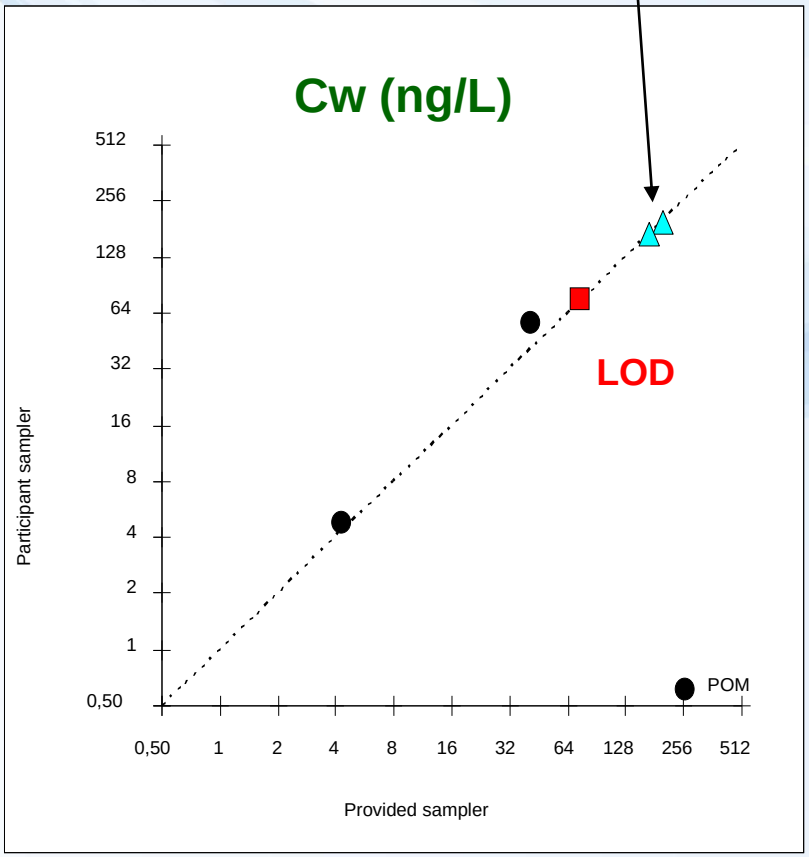
	Participant Sampler Cw ng/L
Median	4.8
s	10.9
GeomMean	5.5
n	3
Outliers	0
Spot samples	
Period 1	198
Period 2	171
LOD	75

Example BPA - Samplers comparison

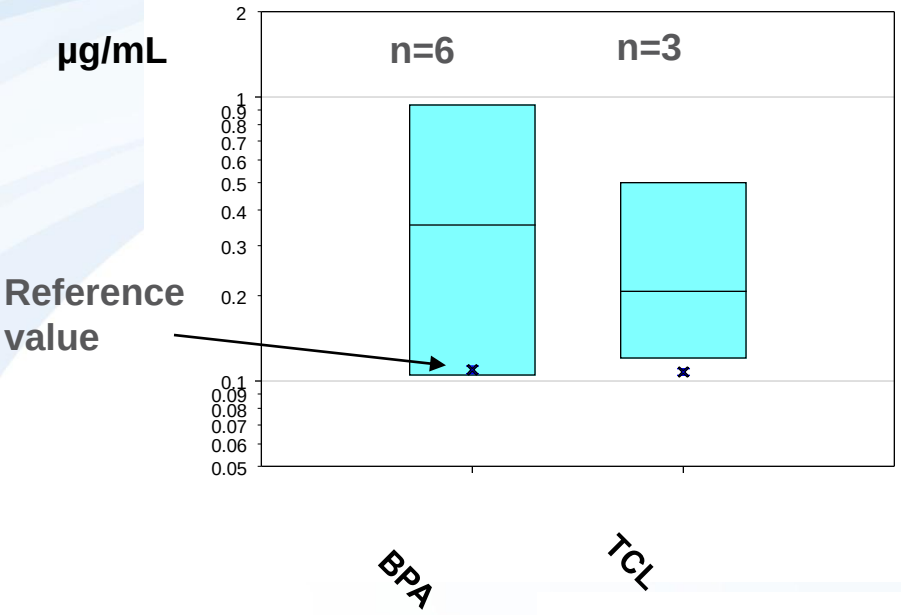
Composite water sample

(2 per exposure)



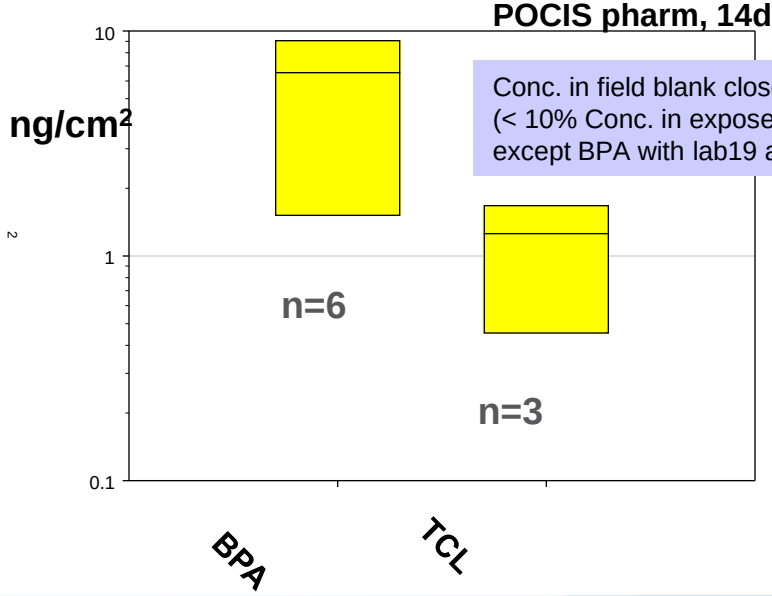


Standard solution, µg/mL



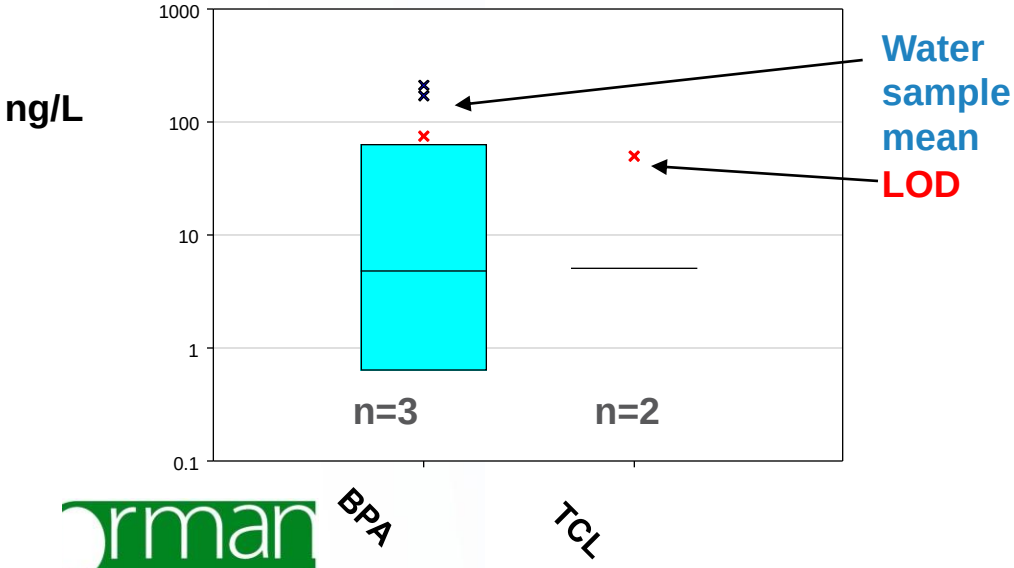
Provided sampler, ng/cm²

POCIS pharm, 14d



Conc. in field blank close to LOD
(< 10% Conc. in exposed samplers, except BPA with lab19 and 20)

Participant sampler, Cw in ng/L



Water composite samples

Sample/Compound	Bottle A1 (20.6.-26.6.)	Bottle A2 (27.6.-4.7.)	units
Triclosan	<50	<50	ng/L
Bisphenol A	206	122	ng/L

Variability of reported results

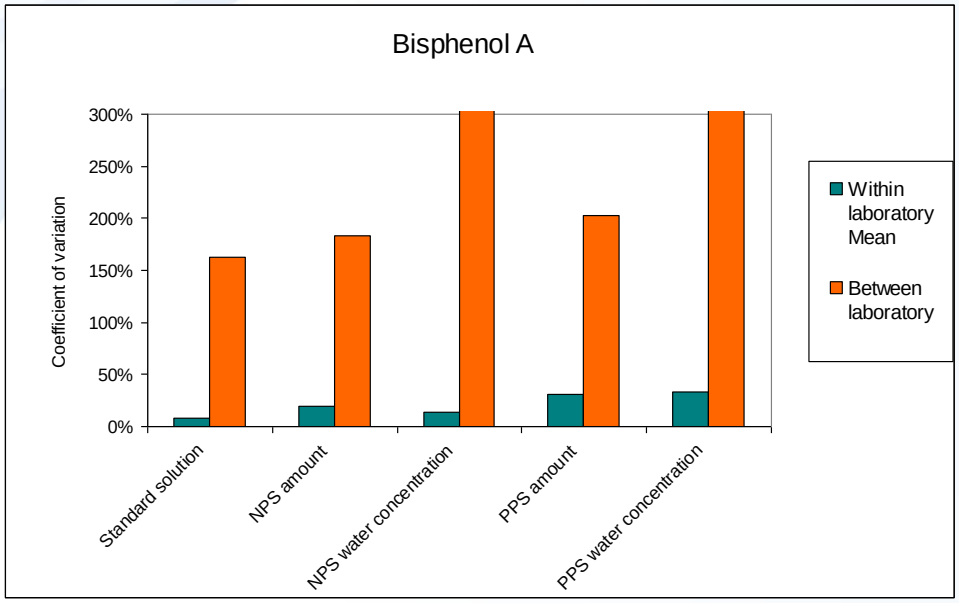
Compound:		Bisphenol A			
			Coefficient of variation (%)		
Variability:		Within laboratory			Between laboratory
Matrix analysed:		Mean	Min.	Max.	
	Standard solution	8%	1%	20%	162%
Provided sampler	NPS amount	19%	5%	36%	183%
	NPS water concentration	14%	5%	30%	>200%
Participant sampler	PPS amount	31%	10%	60%	>200%
	PPS water concentration	33%	6%	60%	>200%

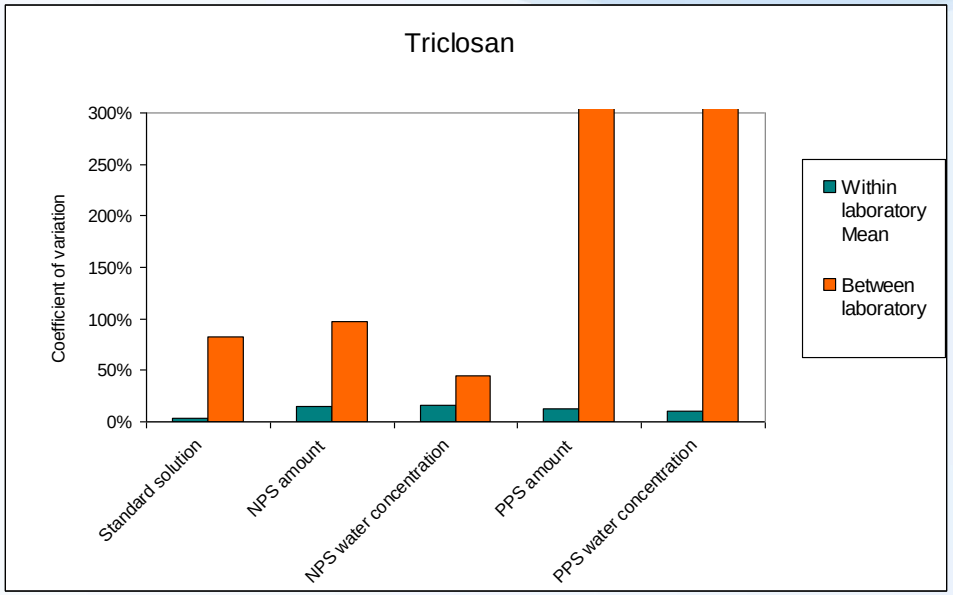
Compound:		Triclosan			
			Coefficient of variation (%)		
Variability:		Within laboratory			Between laboratory
Matrix analysed:		Mean	Min.	Max.	
	Standard solution	3%	0%	8%	82%
Provided sampler	NPS amount	15%	7%	23%	98%
	NPS water concentration	16%	7%	20%	45%
Participant sampler	PPS amount	13%	11%	14%	>200%
	PPS water concentration	11%	10%	11%	>200%

NPS – provided passive sampler; PPS – participant passive sampler

- **A good within laboratory variability in standard solution (mean CV at 8 and 3% for BPA and TCL)**
- **In provided samplers for sampler uptake : a good within laboratory variability (mean CV at 19 and 15% for BPA and TCL) and relatively high between variability (>98%)**
- **In all samplers : no reasonable to evaluate a between laboratory variability for water concentration (n= 3 for BPA, 2 pour TCL)**

Variability of reported results





Conclusions for PFOS/PFOA, BPA and TCL

•Few results on TWA concentration in water ☛ passive sampler calibration is scarce (no calibration data available)

• In provided samplers for sampler uptake (ng/cm^2):

For perfluorinated compounds ☛ a good within laboratory variability (15 to 25%) and acceptable between variability (<51%)

For BPA and TCL ☛ a good within laboratory variability (mean CV at 19 and 15% for BPA and TCL) and relatively high between variability (>98%)

Thank you for your attention

+ 2 × stand. dev. of log_2 transf. data

median

- 2 × stand. dev. of log_2 transf. data

+ expanded uncertainty with $k = 2$

reference value

- expanded uncertainty with $k = 2$

SPMD ← sampler type

← repeatability (± 2 × SD)

← mean value

outlier colour

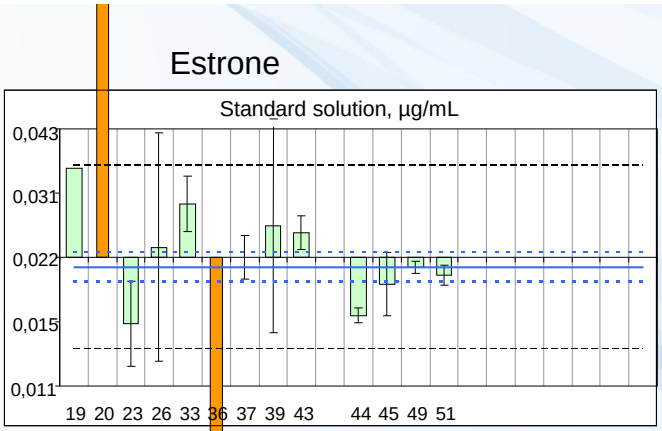
composite water sample (2 per exposure)

water sample mean

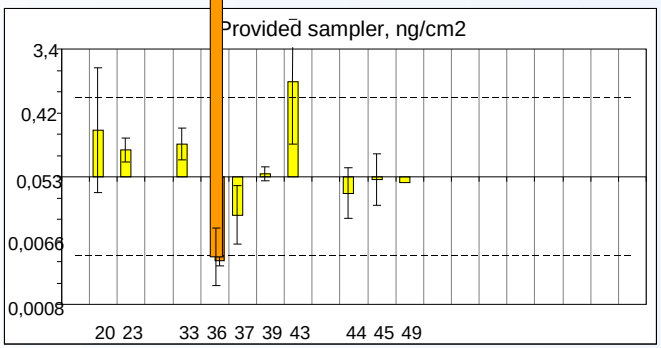
Example :

Estrone

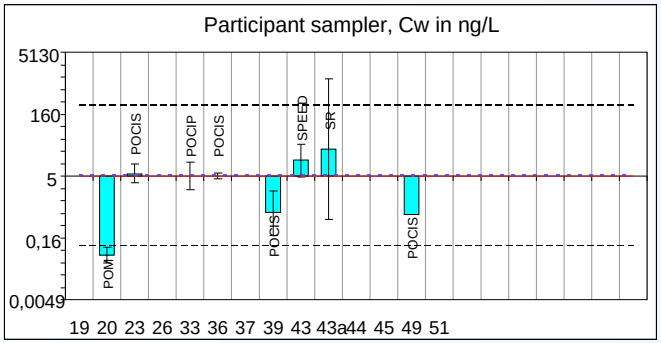
	Stand. Solution µg/mL
Median	0.0217
s	0.021
Geomean	0.022
n	13
Outliers	2
s excl. outl	0.0054
Refvalue	0.02
Exp. Unc	0.00



	Provided Sampler uptake ng/cm2
Median	0.053
s	0.084
Geomean	0.063
n	10
Outliers	1
s excl. outl	0.068



	Participant Sampler Cw ng/L
Median	5.0
s	9.8
GeomMean	2.3
n	8
Outliers	0



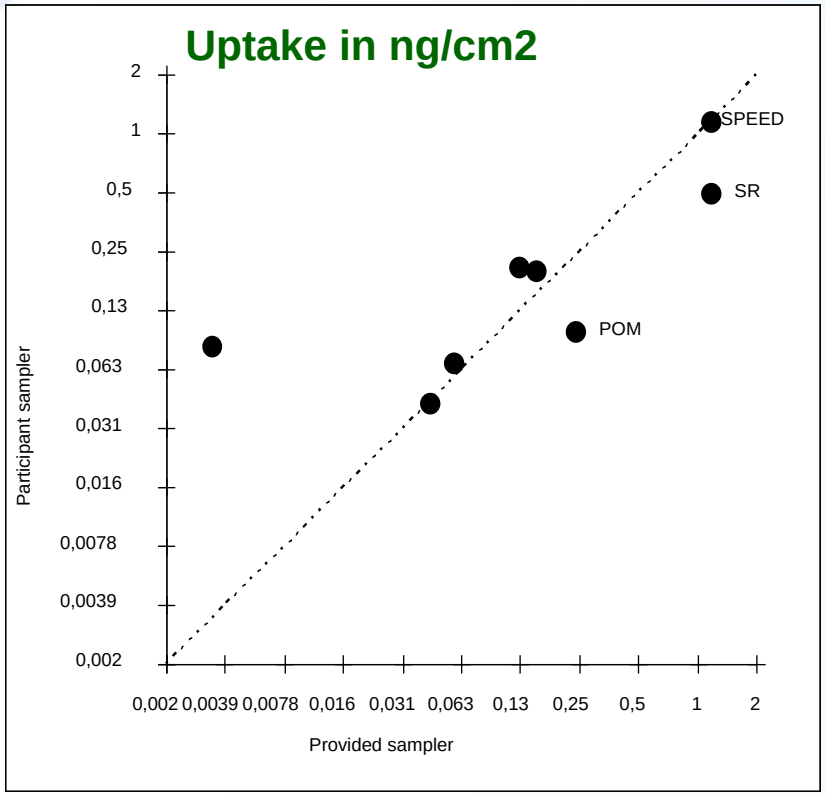
Spot samples

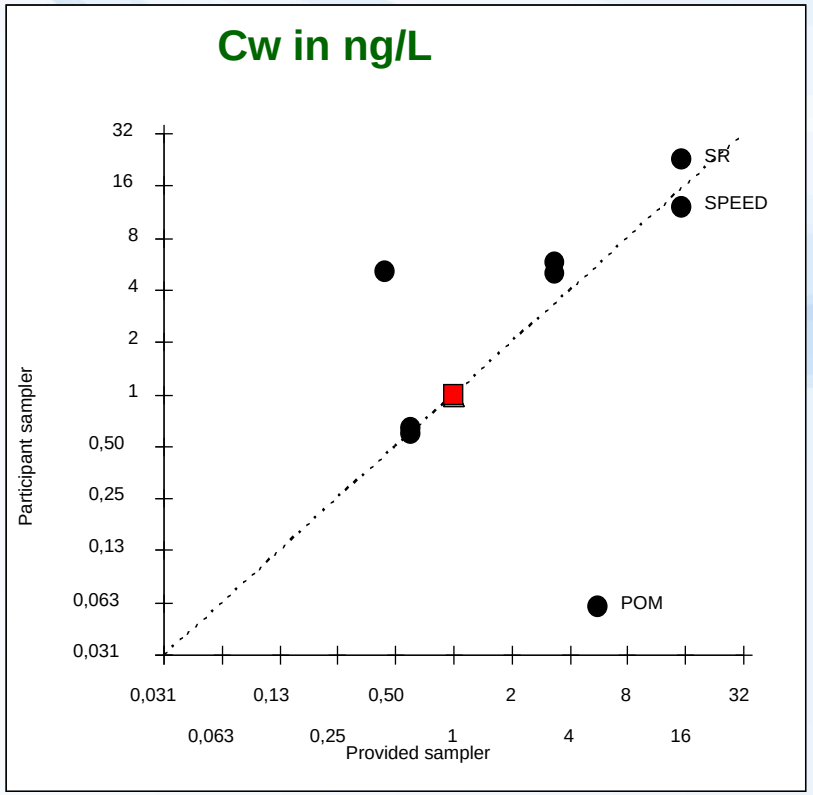
Period 1

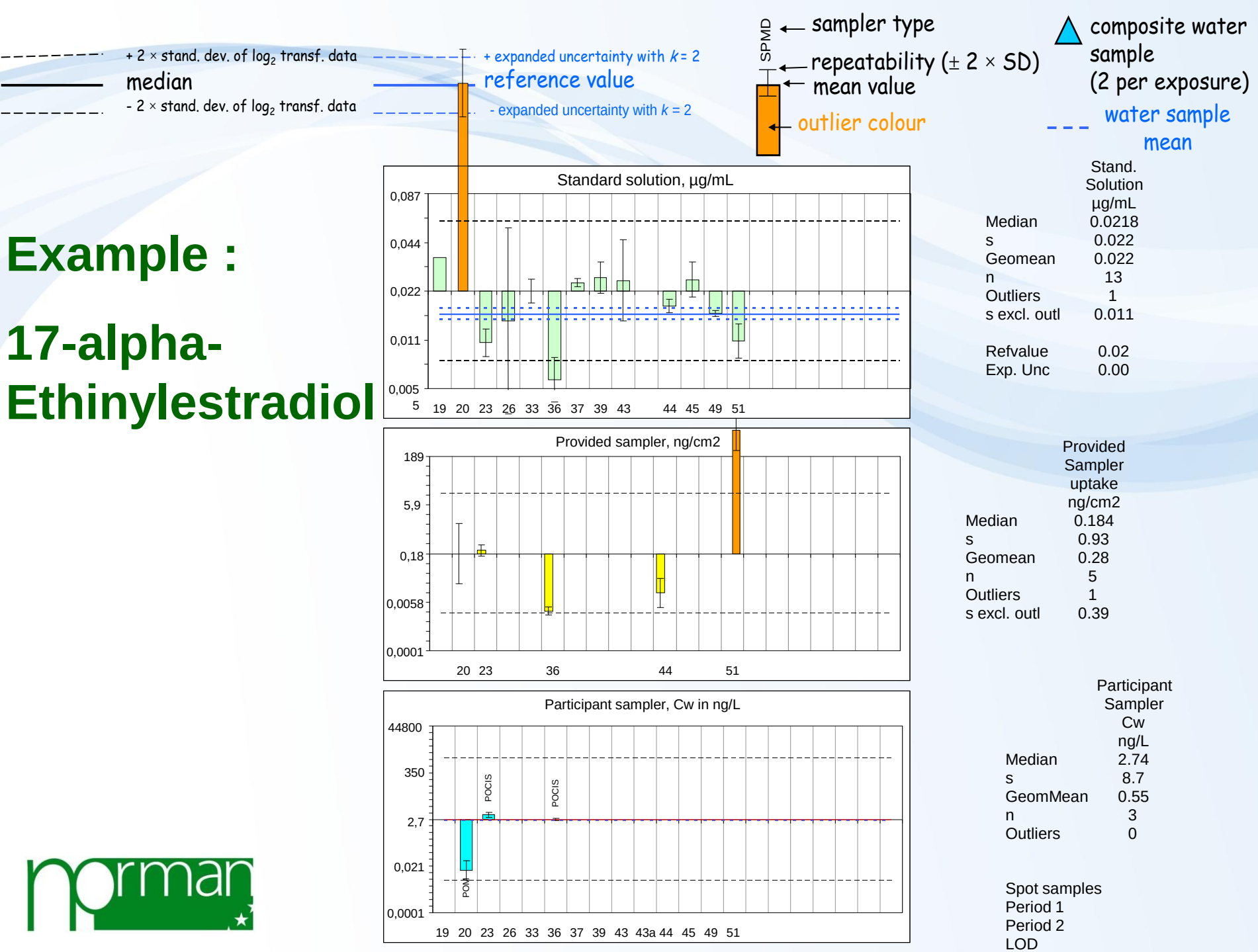
Period 2

LOD

Estrone - Samplers comparison







Example :

17-alpha-Ethinylestradiol

	Stand. Solution µg/mL
Median	0.0218
s	0.022
Geomean	0.022
n	13
Outliers	1
s excl. outl	0.011
Refvalue	0.02
Exp. Unc	0.00

	Provided Sampler uptake ng/cm2
Median	0.184
s	0.93
Geomean	0.28
n	5
Outliers	1
s excl. outl	0.39

	Participant Sampler Cw ng/L
Median	2.74
s	8.7
GeomMean	0.55
n	3
Outliers	0

Spot samples
Period 1
Period 2
LOD

17-alpha-Ethinylestradiol - samplers comparison