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Royal Netherlands Institute for Sea Research

Uncertainties in passive sampling of nonpolar contaminants

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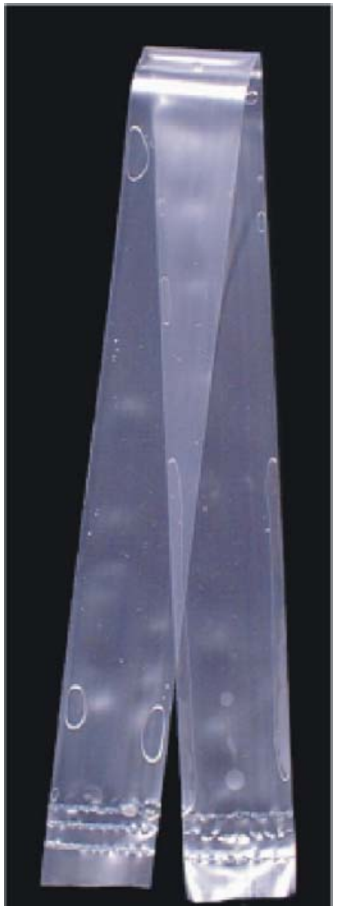
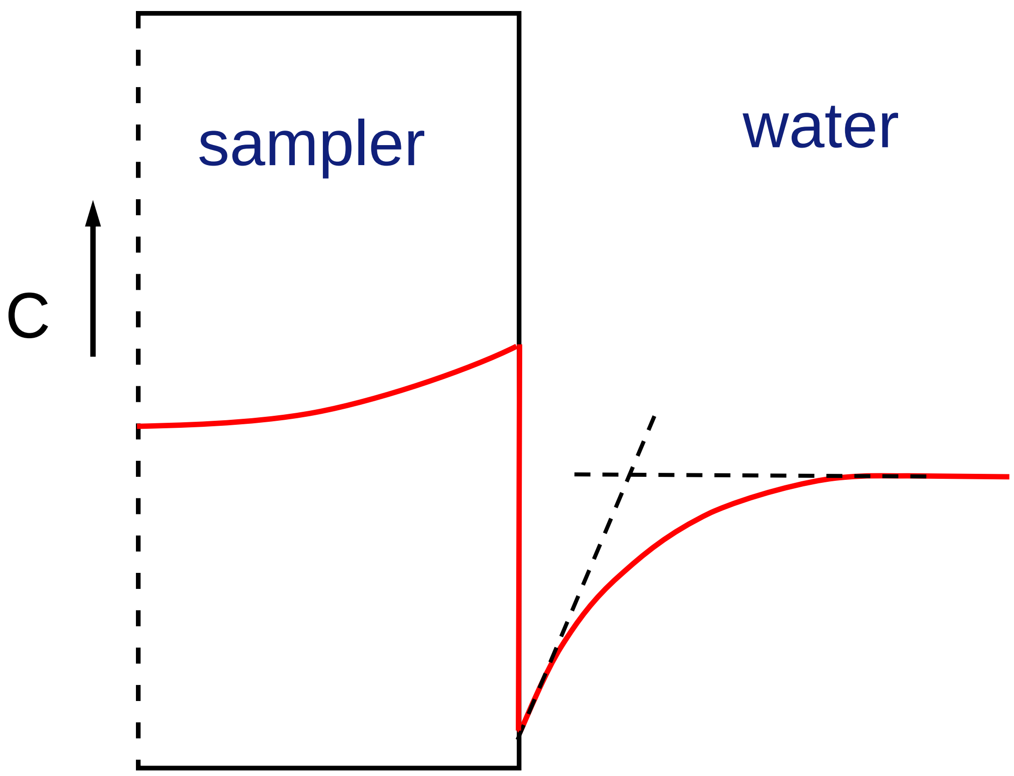
Content

- Uncertainties in principles (concepts, models, principles, theory,....) (vanishingly small errors)
- Precision (small errors)
- Accuracy (moderate errors)
- Interlab variability (substantial errors)



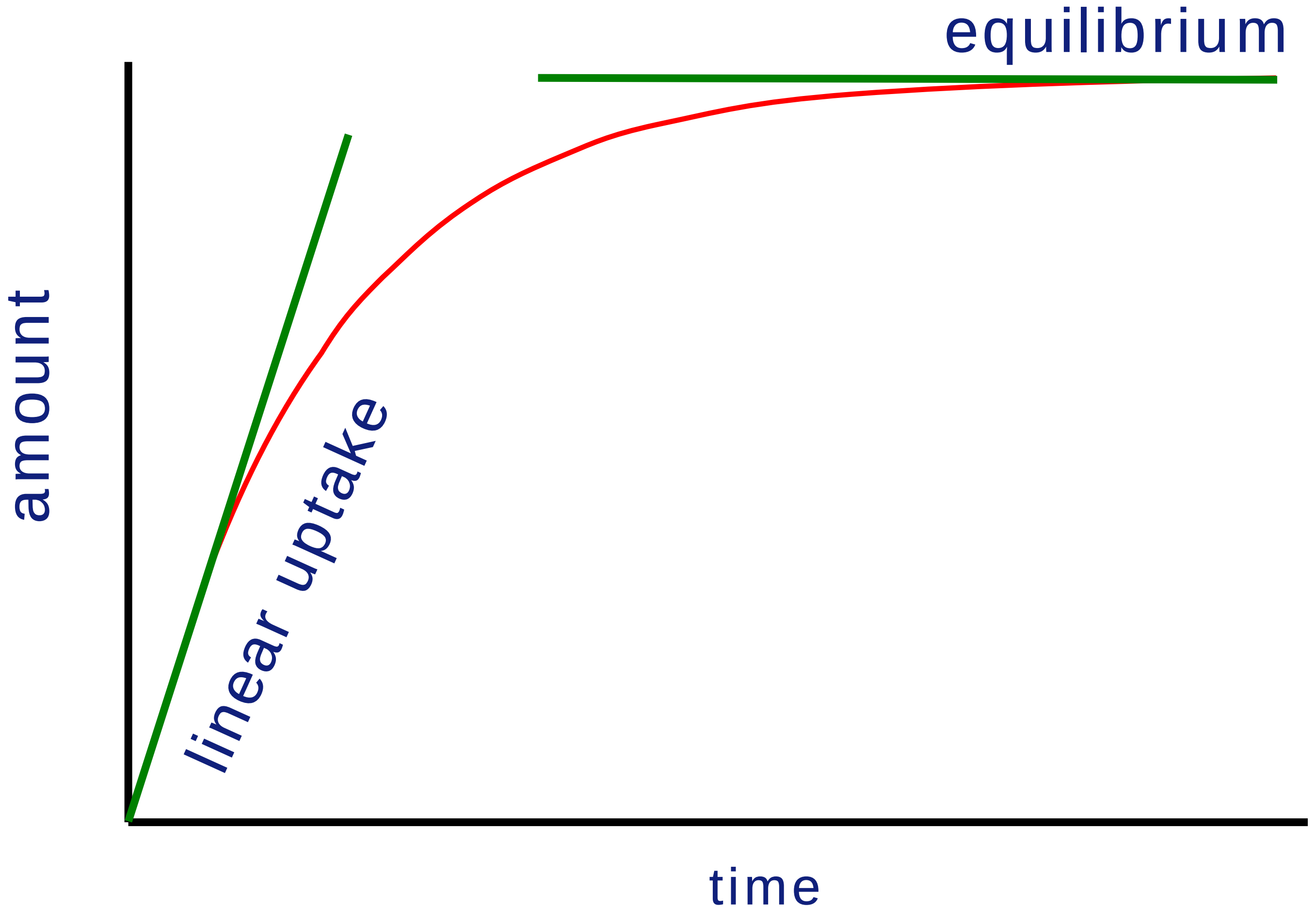
Principles: Working principle



Assumptions:

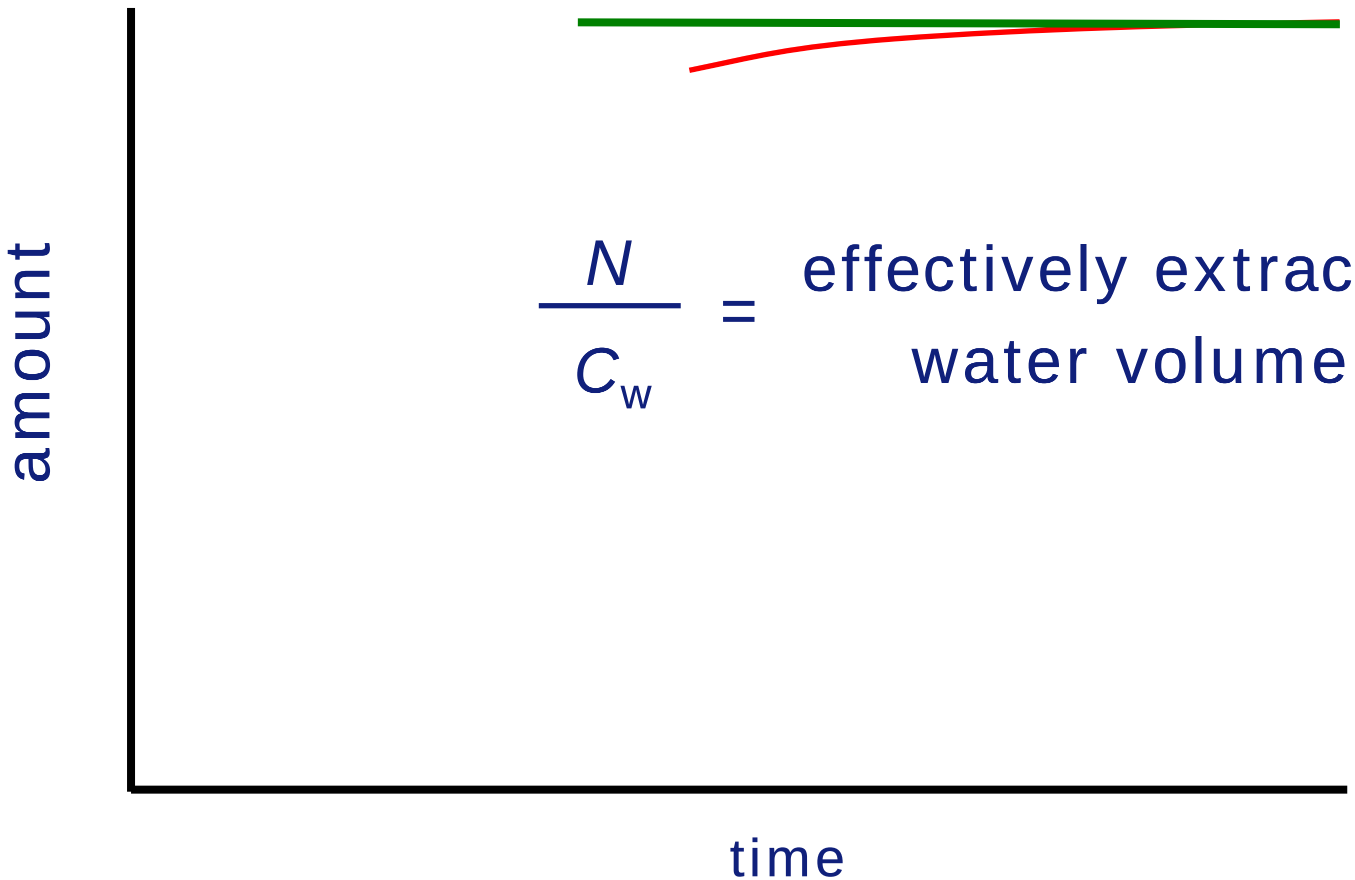
- equilibrium at the interface
- first order transport kinetics
- reversible and linear sorption

Principles: Uptake kinetics



Principles: Equilibrium stage

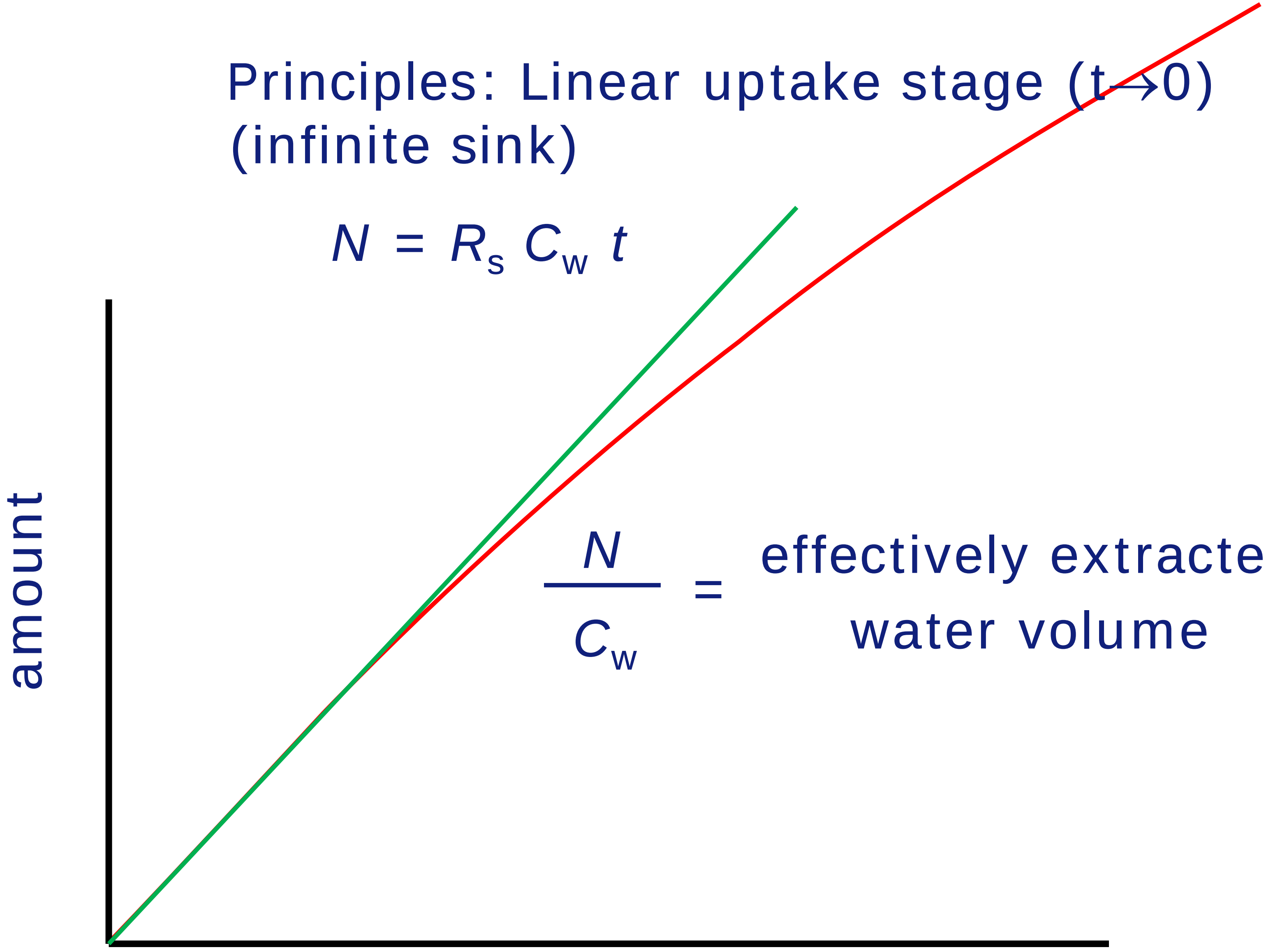
$$\frac{N}{m_s} = K_{sw}\, C_w$$



$$\frac{N}{C_w} = \text{effectively extracted water volume} = m_s\, K_{sw}$$

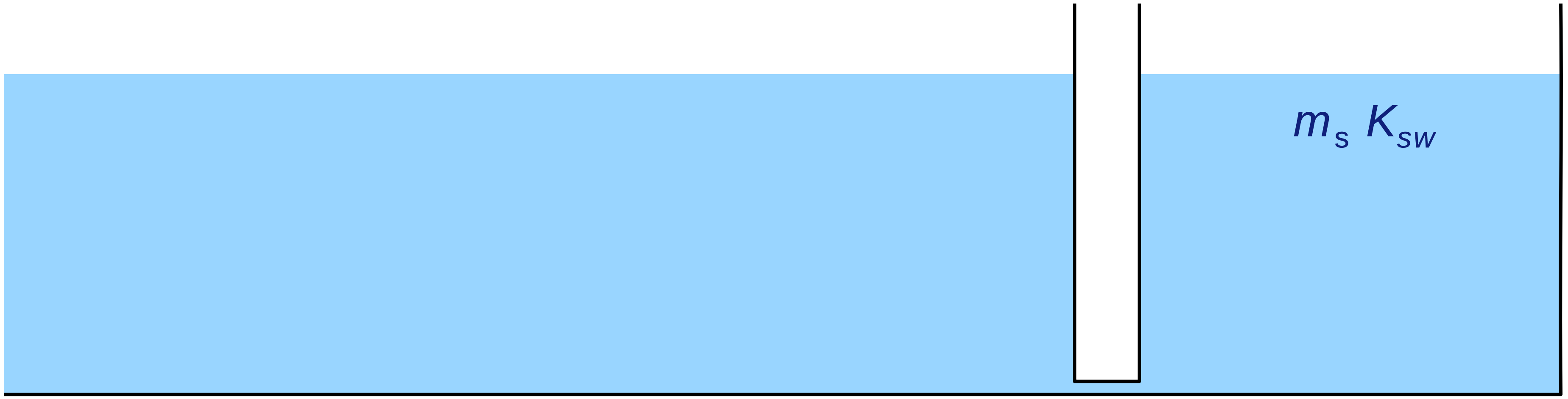
Principles: Linear uptake stage ($t \rightarrow 0$) (infinite sink)

$$N = R_s \, C_w \, t$$



$$\frac{N}{C_w} = \text{effectively extracted water volume} = R_s \, t$$

Principles: Infinite water volume



Sources of variance

$$N = C_{w} \quad K_{sw}\, m_{s}\left[1-\exp\left(-\frac{R_{s}\, t}{K_{sw}\, m_{s}}\right)\right]$$

$t \to 0$: $N = C_{w}\, R_{s}\, t$ (linear stage)

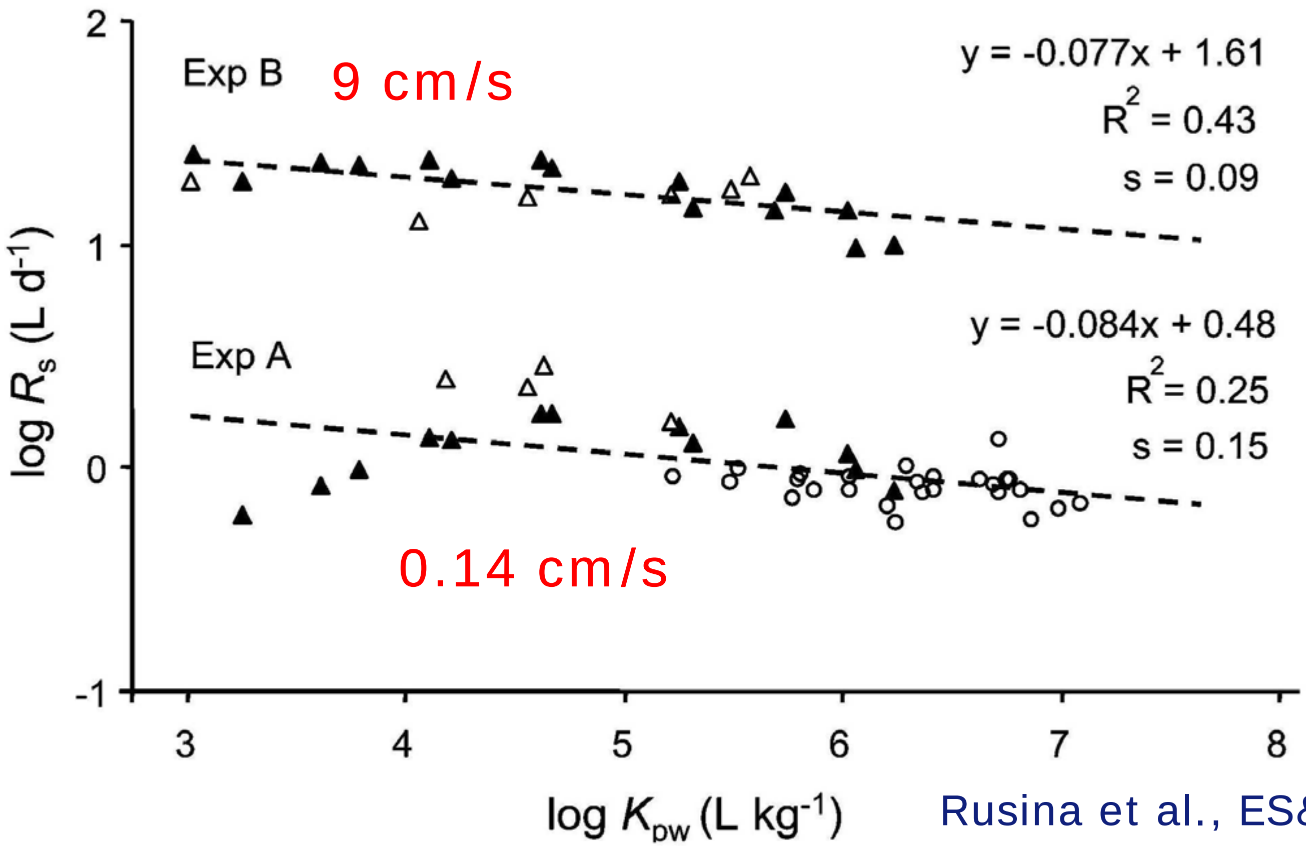
$t \to \infty$: $N = C_{w}\, m_{s}\, K_{sw}$ (equilibrium stage)

Uncertainties from

- N
- R_{s}
- K_{sw}

Sampling rates (R_s)

- compound properties (diffusion coefficient, hydrophobicity)
- temperature
- flow rate
- suspended solids concentration



Rusina et al., ES&T 44:362–367, 2010

Sampling rate model is needed (high-K_{ow})

WBL-controlled uptake

R_s calibration: PRC with $4 < \log K_{ow} < 6.5$

R_s of high K_{ow} compounds?

Hydrodynamics and engineering lit.: $R_s \sim D_w^{2/3}$

$R_s \sim$	pyrene/PCB180 R_s ratio
$MW^{-0.35}$	1.3
$V_{LeBas}^{-0.39}$	1.2
$K_{ow}^{-0.044}$	1.2
$MW^{-0.47}$	1.4
$K_{pw}^{-0.08}$	1.5

< 25%

Uncertainties from lack of understanding:

- Maybe < 25% for R_s extrapolation into high K_{ow} range

Precision: R_s calibration (~20%)

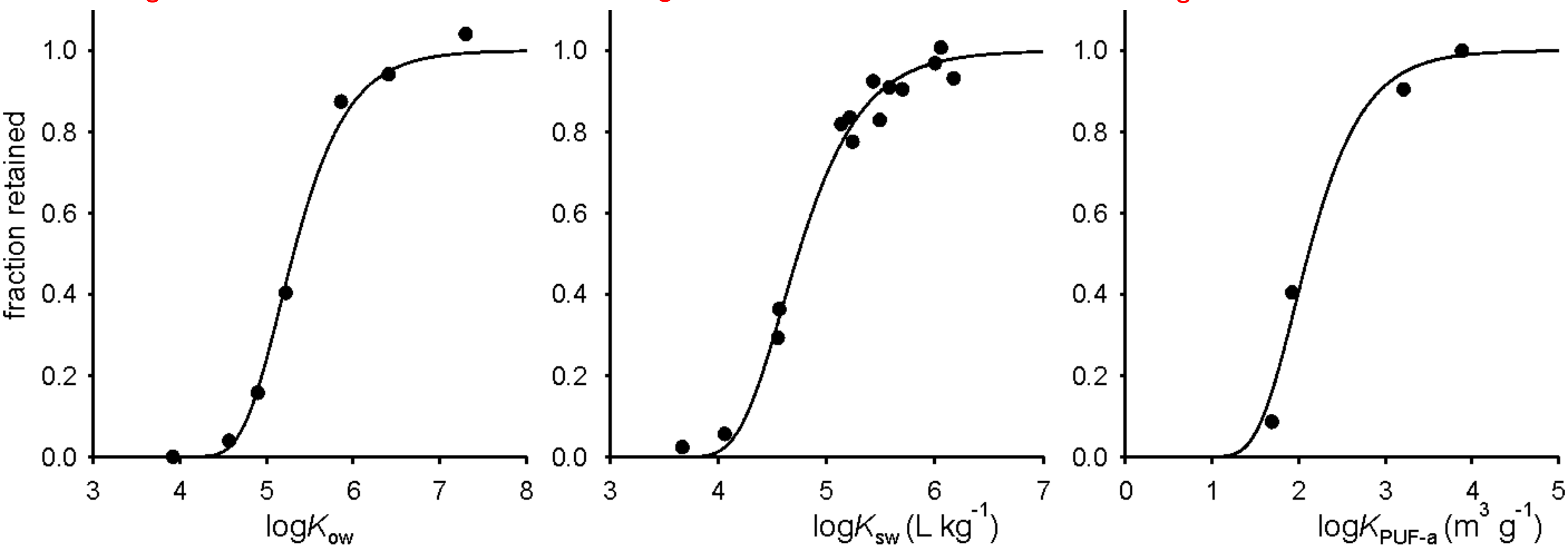
Performance reference compounds (PRCs)

- not occurring in the water
- spiked into PSD before exposure
- dissipation follows: $\dfrac{N_s}{N_0} = \exp\left(-\dfrac{R_s\ t}{K_{sw}\,V_s}\right)$

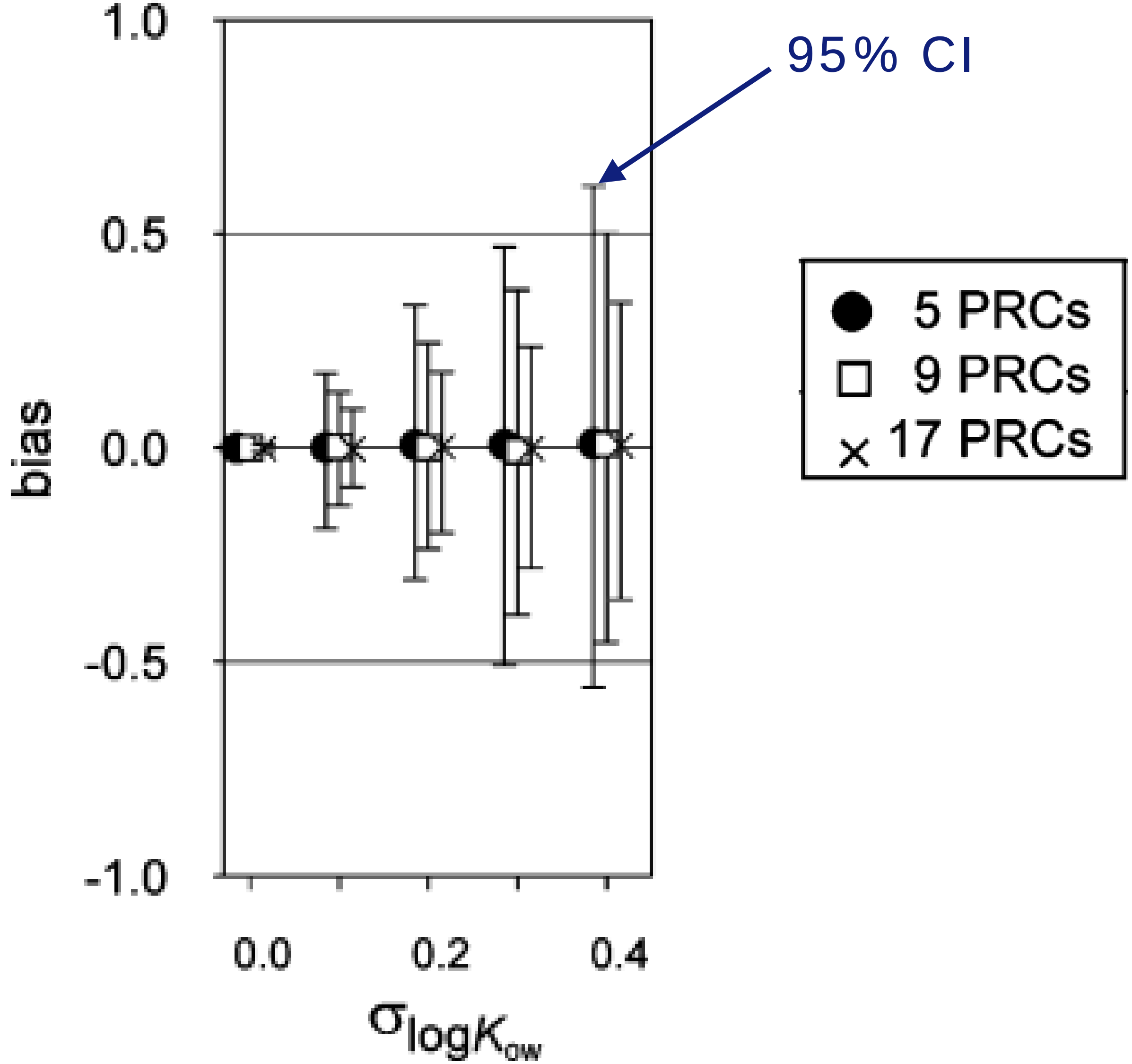
SPMD in water $R_s = 5.1 \pm 0.3$ L d^{-1}

silicone in water $R_s = 11.6 \pm 0.7$ L d^{-1}

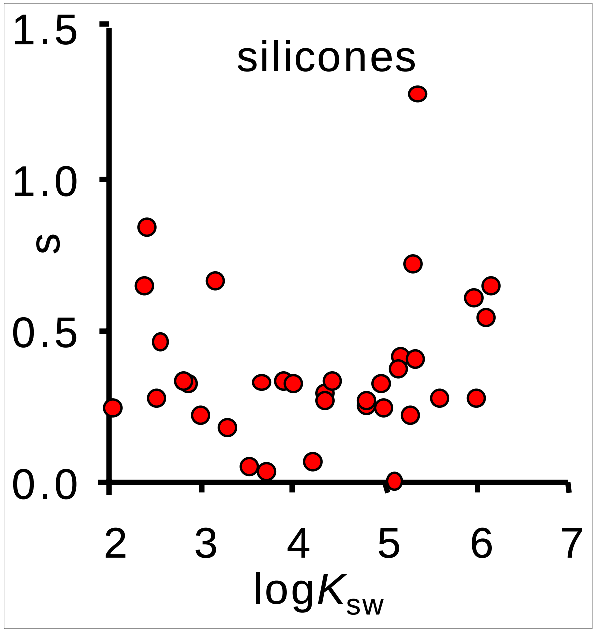
PUF in air $R_s = 5.6 \pm 0.6$ m^3 d^{-1}

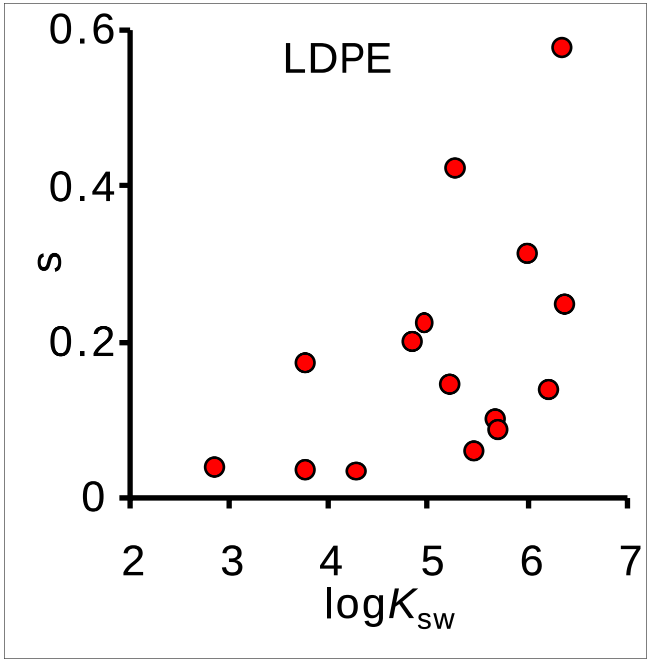


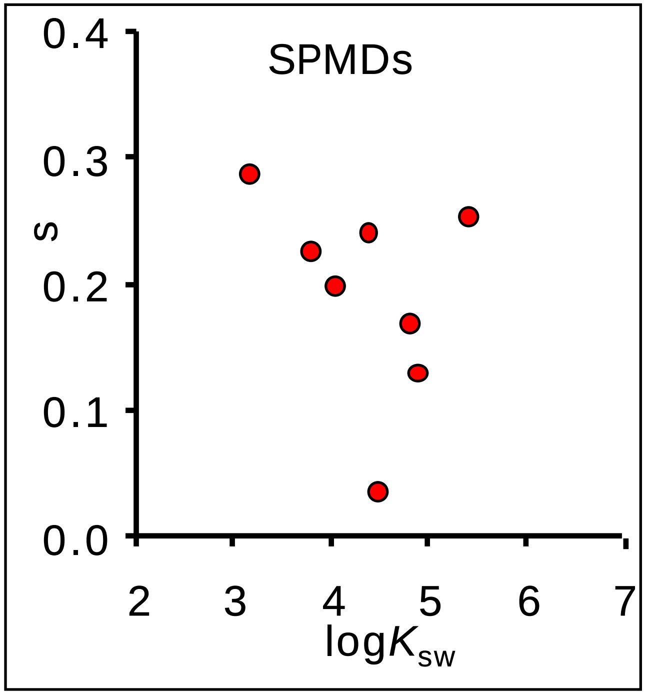
Accuracy: R_s calibration



Accuracy: K_{sw} calibration







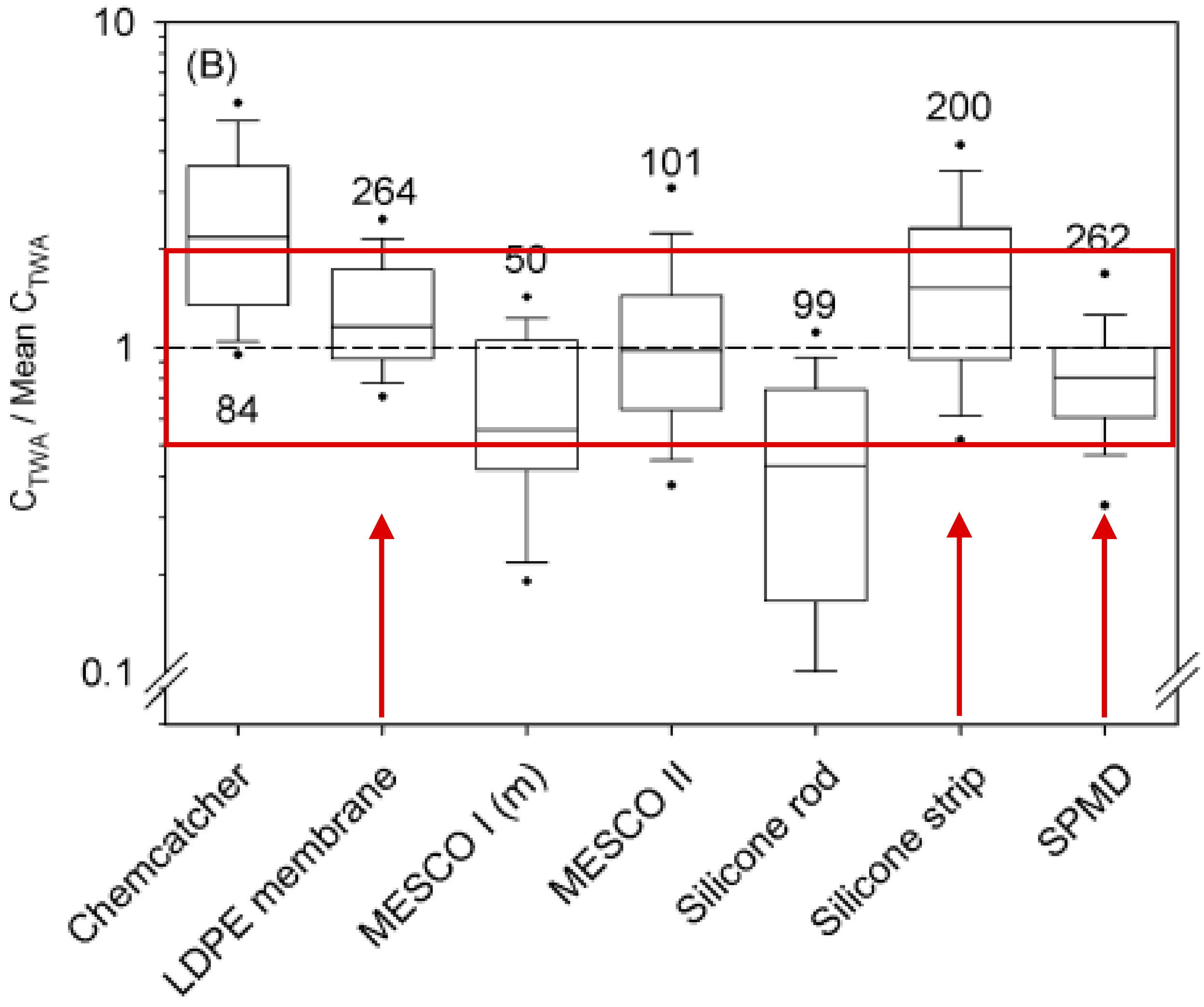
Kinetic and equilibrium sampling

- Kinetic: $N = C_w R_s t$
  R_s precision: <20%
  R_s bias ~ 0.2 log units (factor 1.6) from K_{sw} of PRCs
  R_s bias from R_s extrapolation to high K_{ow} compounds <25%

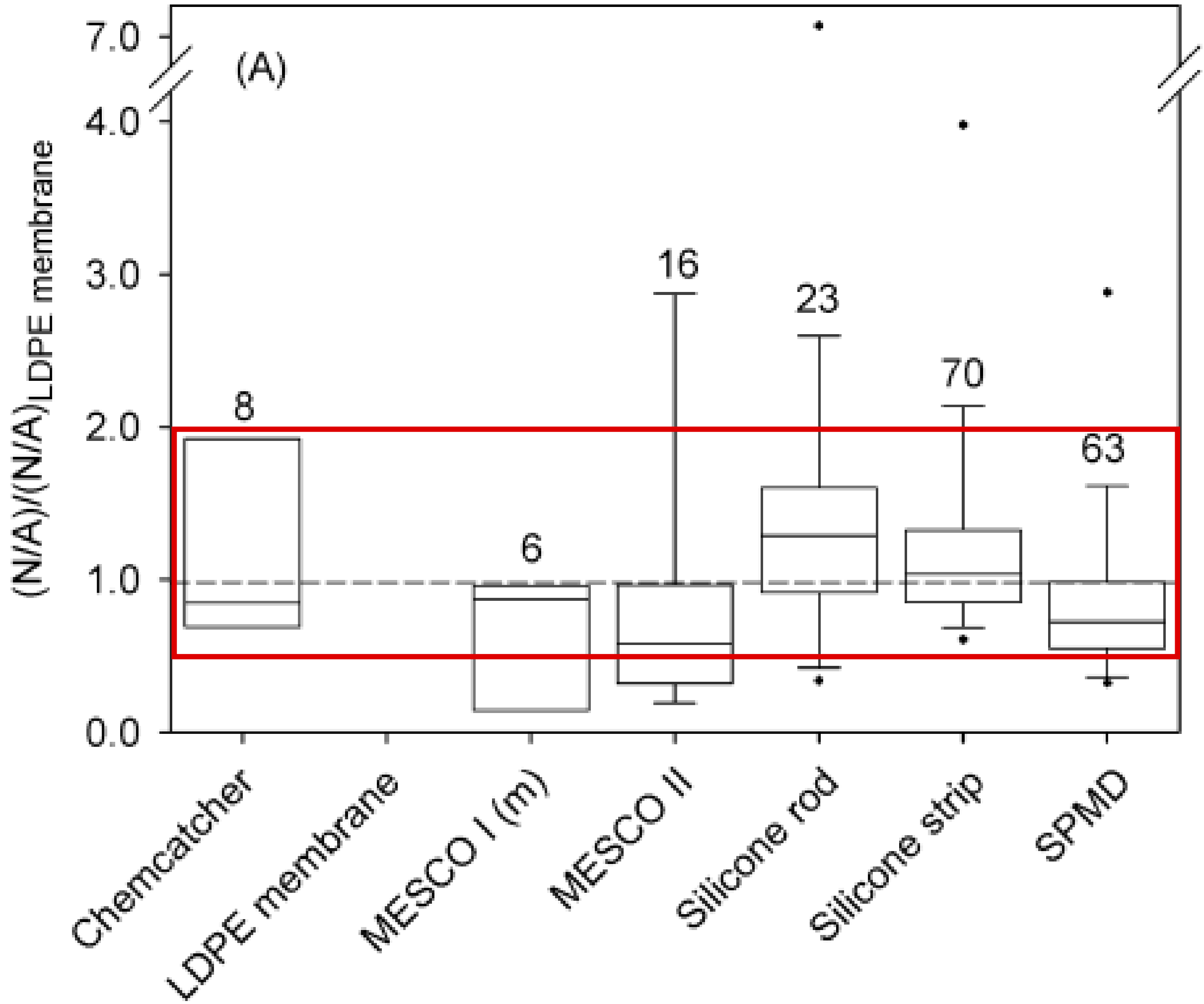
- Equilibrium: $N = m K_{sw} C_w$
  C_w bias from analyte K_{sw} = 0.2 log units (factor 1.6)

- Comparison among samplers ~ 0.25 log units (factor 1.7)

Interlab + intersampler variability
Allan et al. 2009



Analytical interlab variability
Allen et al. 2009



Within lab variability + temporal variability (3 consecutive 6-wk silicone exposures Smedes, Beeltje, Jonker (2012)

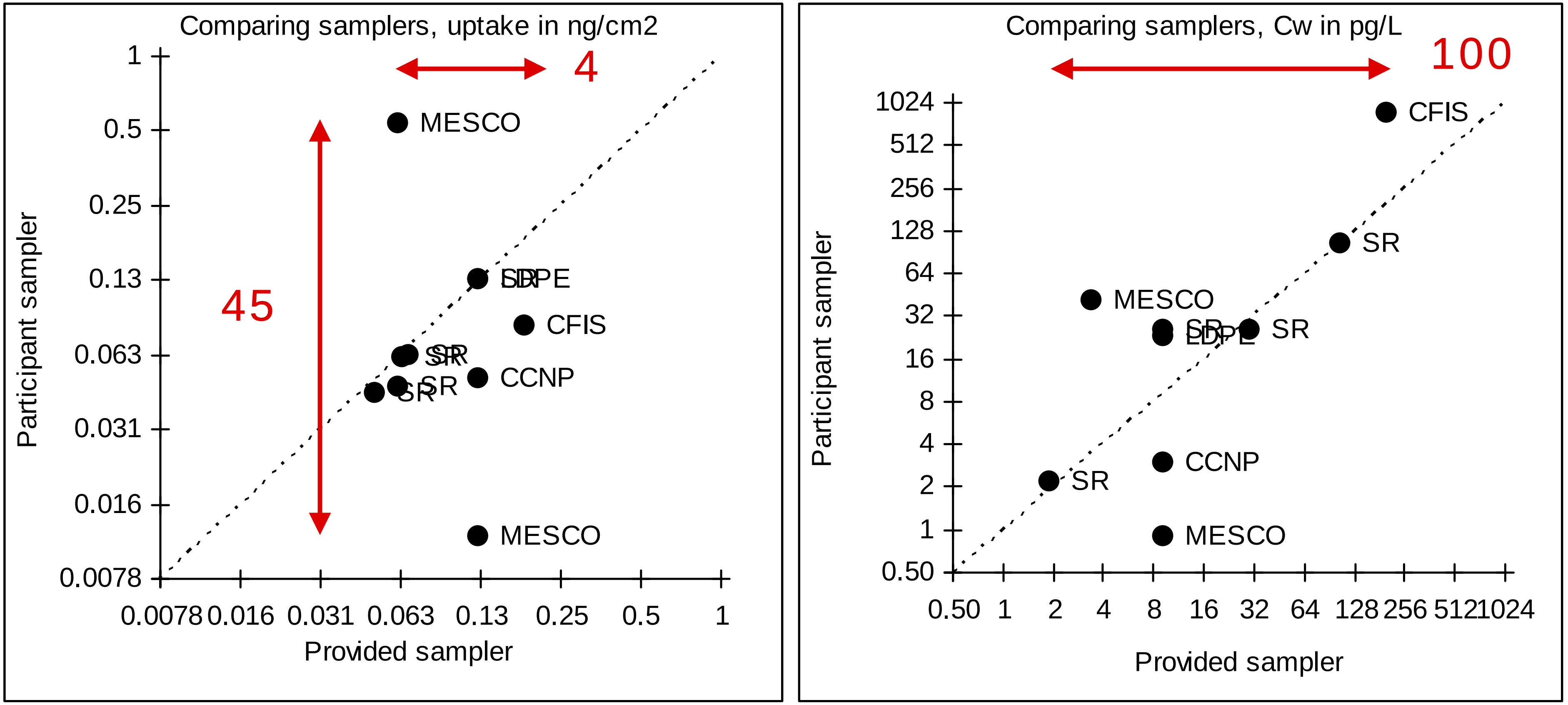
propiconazool (som)	9
anthraquinone	12
atrazine	13
phantolide (AHMI)	14
tebuconazool	14
diuron	16
PCB-28	16
diflufenican	16
desmetryn	17
lindaan	17
hexachloorbenzeen	17
chryseen	17
galaxolide (HHCB)	18
boscalid	18
antraceen	19
PCB-52	19
linuron	19

tonalide (AHTN)	19
difenoconazool (som)	20
fenarimol	20
benzo(b)fluoranteen	20
cyprodinil	20
indeno(123-cd)pyreen	20
imazalil	20
PCB-118	21
diazinon	21
benzo(a)antraceen	21
benzo(a)pyreen	21
PCB-101	21
PCB-180	21
azoxystrobin	22
traseolide (ATTI)	22
acenaftyleen	22

PCB-153	22
isoproturon	23
benzo(ghi)peryleen	23
PCB-138	23
benzo(k)fluoranteen	24
pyreen	24
pentachloorbenzeen	25
fluoranteen	28
fenantreen	28
dibenzo(ah)antraceen	28
broompropylaat	29
DEET	29
prometryn	30
terbutryn	31
pyrimethanil	31
carbendazim	34

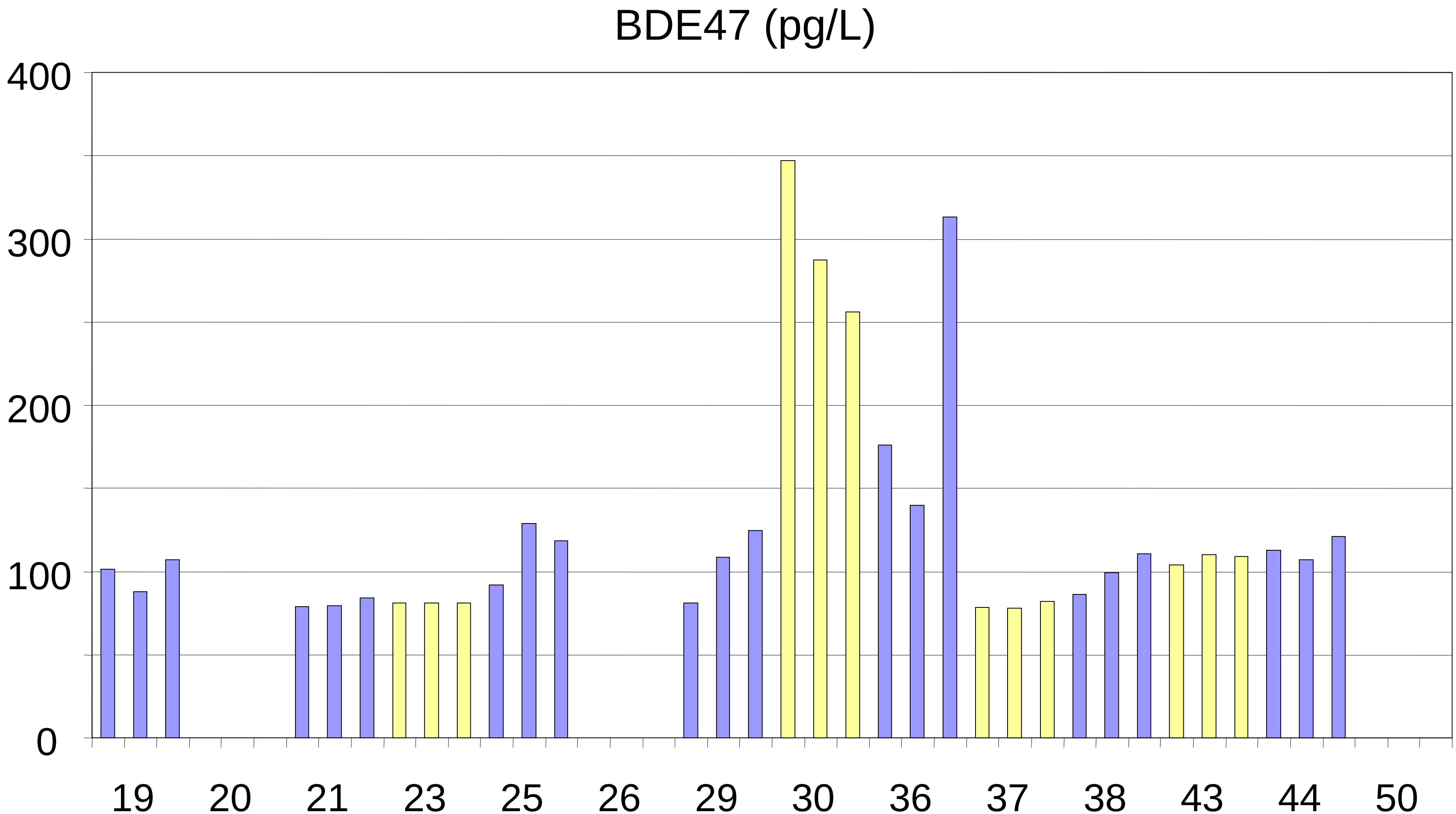
fluoreen	36
fenpropimorf	41
chloorpyrifos-ethyl	41
hexachloorbutadieen	41
pendimethalin	42
celestolide (ADBI)	42
acenafteen	45
tri-allaat	52
terbutylazine	53
propazine	53
cashmeron (DPMI)	61
naftaleen	64
procimidon	65
dimethenamid (-P)	72
prosulfocarb	74
metolachloor (-S)	84

NORMAN ILS: BDE sampling



- anlytical: ~ factor 4
- calculation + analytical: factor 100

NORMAN ILS: C_w calculated by organiser, based on chemical analysis by participants



Conclusions

- PS for nonpolars is well understood, including the uncertainties
- Precision (R_s) < 20 %
- Accuracy ~ 0.2 log units
  - high K_{ow} range (>6): K_{sw} of PRCs
  - low K_{ow} range (<4): K_{sw} of target analytes
- Much to be gained from reducing interlab variability
  - analytical (target analytes and PRCs)
  - calculation mistakes
  - K_{sw} determination