Specimen banking of passive samplers for aquatic environments: purpose, possibilities and procedures

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Specimen banking of passive samplers (PS)?

No specimen banks currently include PS!

Surely passive samplers has to be the optimum matrix for specimen banking!

why?

- Difficult to specimen bank water, easier with biota or sediment but still requiring manipulation without blanks
- Possibility to use proper blanks/control samplers, so better traceability
- Don’t take much space in the freezer

What’s different from «regular» SB matrices?

- PS is not a environmental matrix but a manufactured device
  - Selectivity from the onset of PS
  - How much chemical is in the sampler after exposure depends on the sampler configuration and sampling operation
- The availability of blanks and preparation and field control samplers
  - Almost identical treatment of control and exposed samplers can be achieved (preparation, deployment/retrieval, surface cleaning and storage)
  - More than one control sampler for every exposed sampler may be needed
- The possibility to use «reference materials» and spiked polymers for stability studies
- Requires additional information to estimate an environmental concentration
  - Most robust procedure is to obtain this information for each individual sampler
  - Requires the user to estimate a sampling rate unless only qualitative data is needed
- Low volume and ease of storage

Principle of passive sampling (in water)

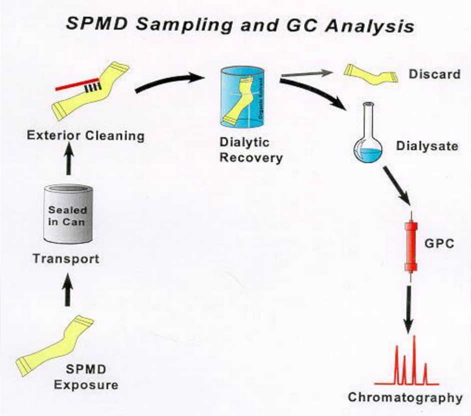
Sampler selection

Sampler deployment

Exposure for days-months

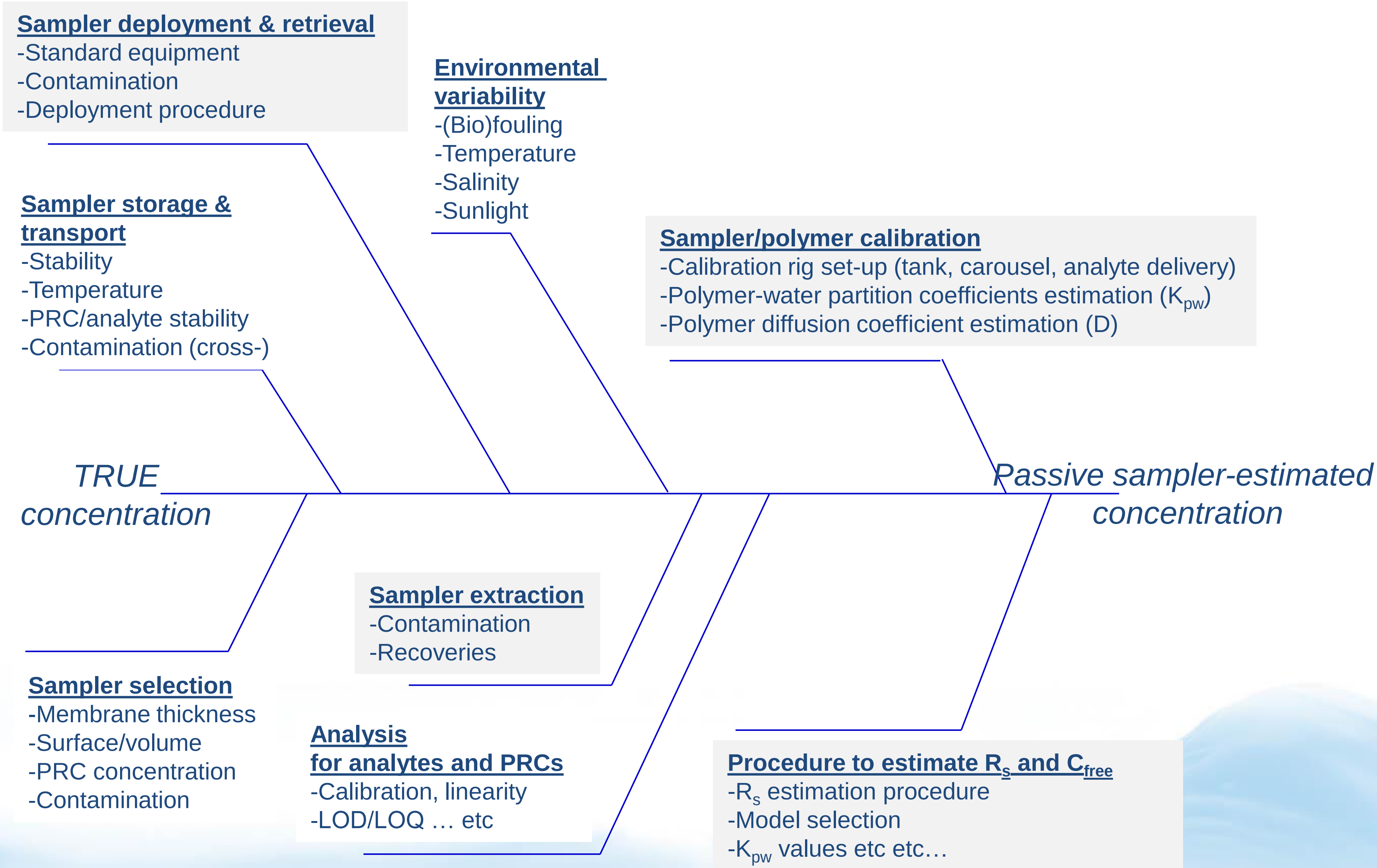
Sampler Retrieval

Sampler Extraction and analysis



Modelling…

Calculation of concentration, C_W


Sampler deployment & retrieval
-Standard equipment
-Contamination
-Deployment procedure
Environmental variability
-(Bio)fouling
-Temperature
-Salinity
-Sunlight
Sampler storage & transport
-Stability
-Temperature
-PRC/analyte stability
-Contamination (cross-)
Sampler/polymer calibration
-Calibration rig set-up (tank, carousel, analyte delivery)
-Polymer-water partition coefficients estimation (K_{pw})
-Polymer diffusion coefficient estimation (D)
TRUE concentration
Passive sampler-estimated concentration
Sampler extraction
-Contamination
-Recoveries
Sampler selection
-Membrane thickness
-Surface/volume
-PRC concentration
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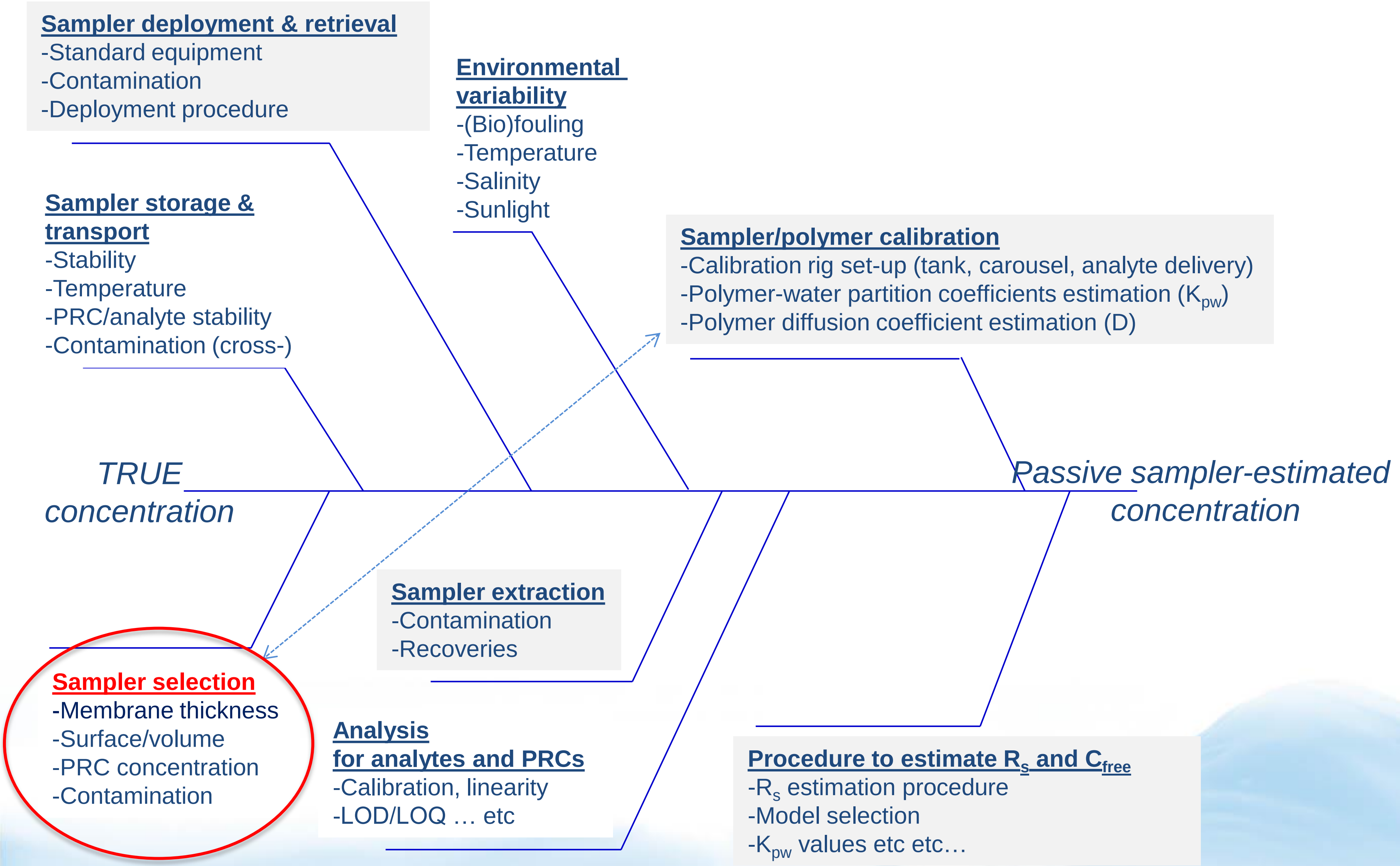
Analysis for analytes and PRCs
-Calibration, linearity
-LOD/LOQ … etc
Procedure to estimate R_s and C_{free}
-R_s estimation procedure
-Model selection
-K_{pw} values etc etc…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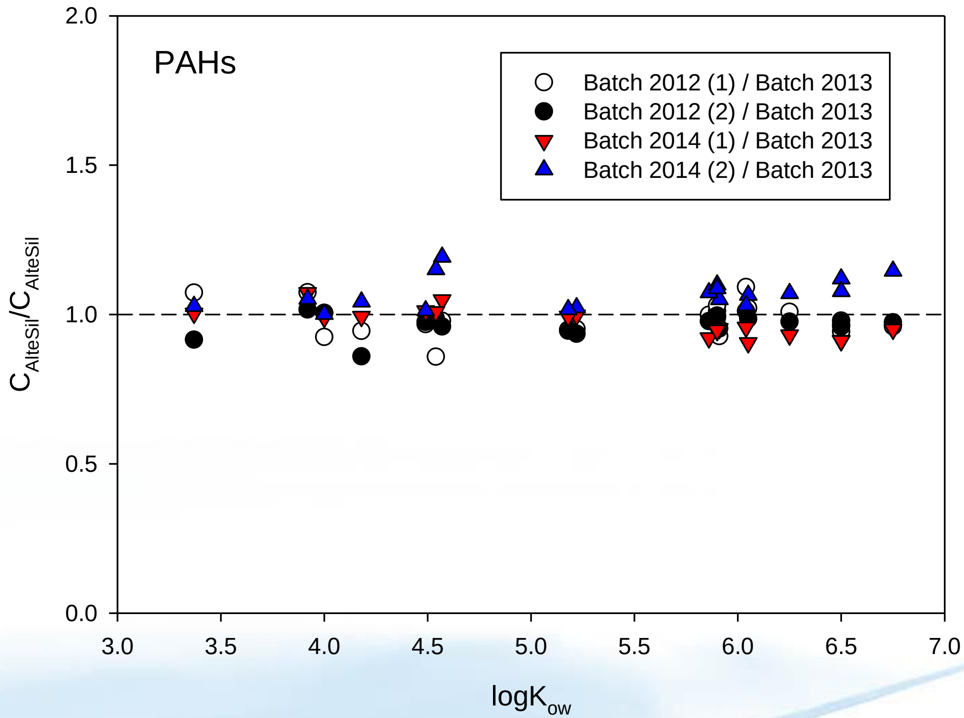
Polymer selection for hydrophobic contaminants

Polymer selection (absorption-based passive sampling):

– Availability, practicality and cost, consistency of the supply

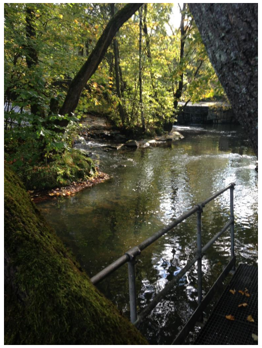
AlteSil™ silicone rubber sheets from different batches equilibrated in 60:40 methanol-water solution



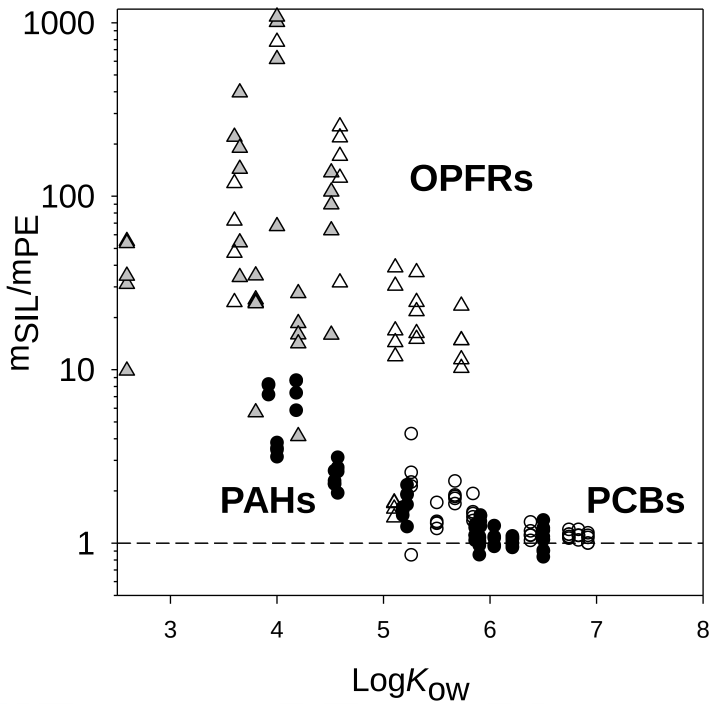
Polymer selection for hydrophobic contaminants

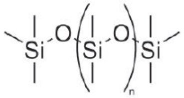
Polymer selection (absorption-based passive sampling):

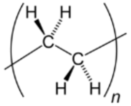
- Sufficiently permeable for compounds of interest
- High pre-concentration factor (high sampler-water partition coefficient)



River Alna

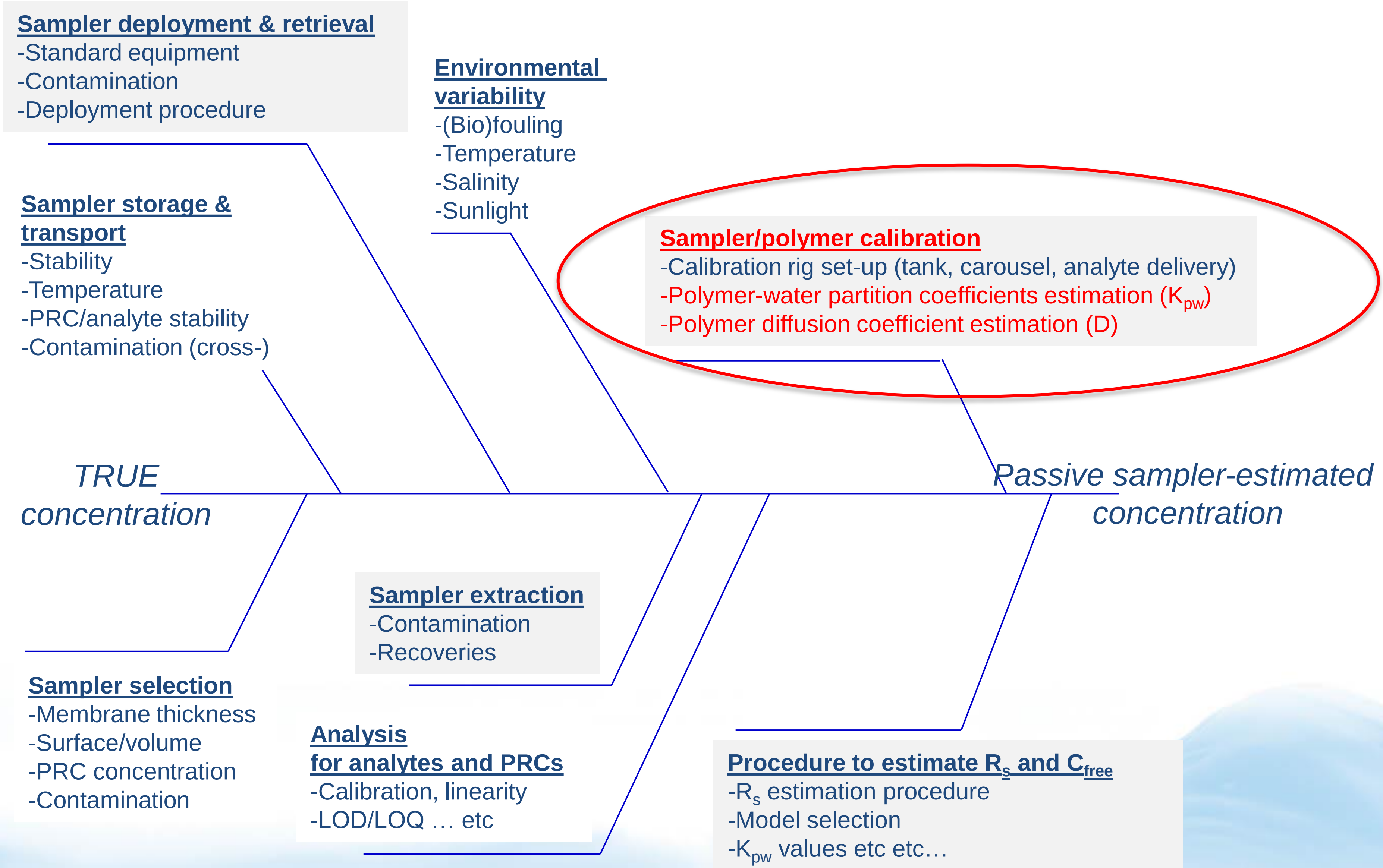






	Silicone rubber	LDPE
Mass (g)	8.5	1.1
Surface area (cm^2)	300	300

*Allan *et al.*, 2013. Passive sampling for target and nontarget analyses of moderately polar and nonpolar substances in water. *Environmental Toxicology and Chemistry* 32, 1718-1726.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Calibration for emerging contaminants

- 33 chemicals of emerging concern (CECs)
- Focus on using single phase samplers (silicone rubber and LDPE)
- Polymer calibration*:
  - Polymer diffusion coefficients, D_p with a film stack experiment
  - Polymer-water partition coefficients, K_{pw} measurement with validation using a co-solvent method

*Pintado-Herrera, Lara-Martín, González-Mazo, and Allan. Determination of silicone rubber and low density polyethylene diffusion and polymer-water partition coefficients for emerging contaminants. *In press in ET&C*, 2015

Calibration data for 33 CECs

Example of measurement in the River Alna (Oslo)

$\log D_p$ $\log K_{pw}$

A

Silicone rubber

MW

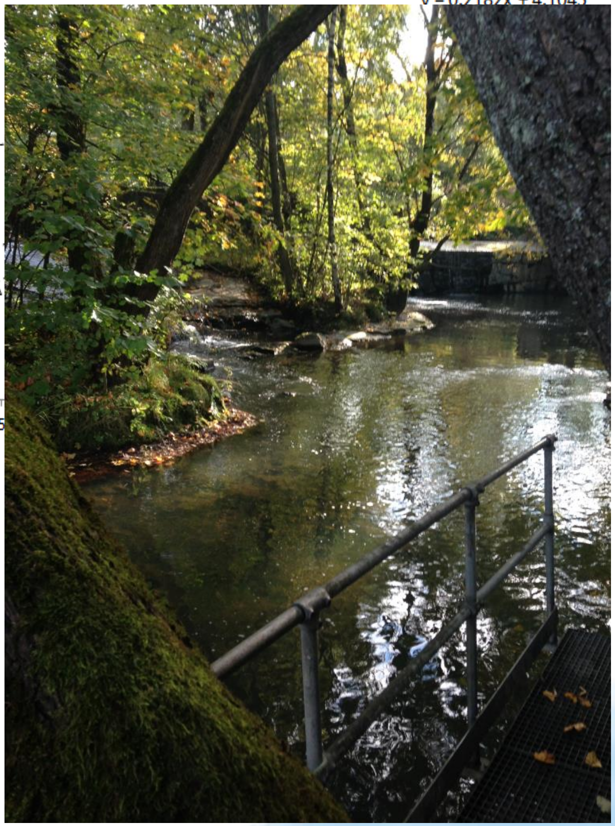
0 100 200 300 400 500

◇ OPCs ○ Fragrances △ UV Filters

OPCs

y = 0.2182x + 4.1045

Chemical		C_{free} (ng L^{-1})
Galaxolide	Synthetic musk	1600
Tonalide	Synthetic musk	51
Oxybenzone	UV filter	108
Octocrylene	UV filter	448
Triclosan	Antibacterial	9
2-ethylhexyl-4-methoxycinnamate	UV filter	4
Triphenylphosphate	Flame retardant/plasticiser	170



Log Dp

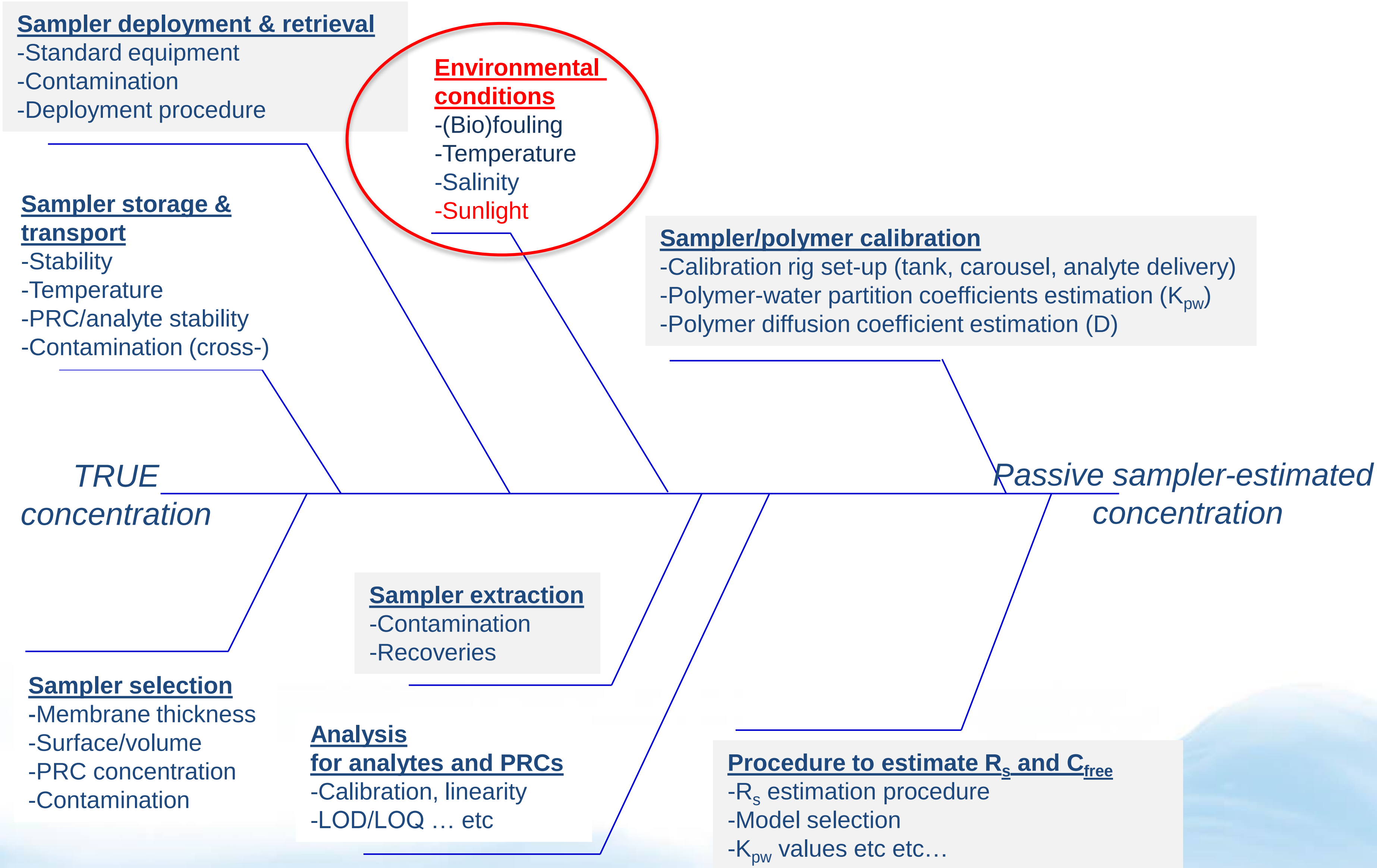
B

4 4.5 5

▲ Endocrine disruptor compounds ▫ UV filters out-of-range

● UV filters ○ OC pesticides (Hale et al. 2010)

◆ Fragrances ■ OPCs + OPCs lower detection limits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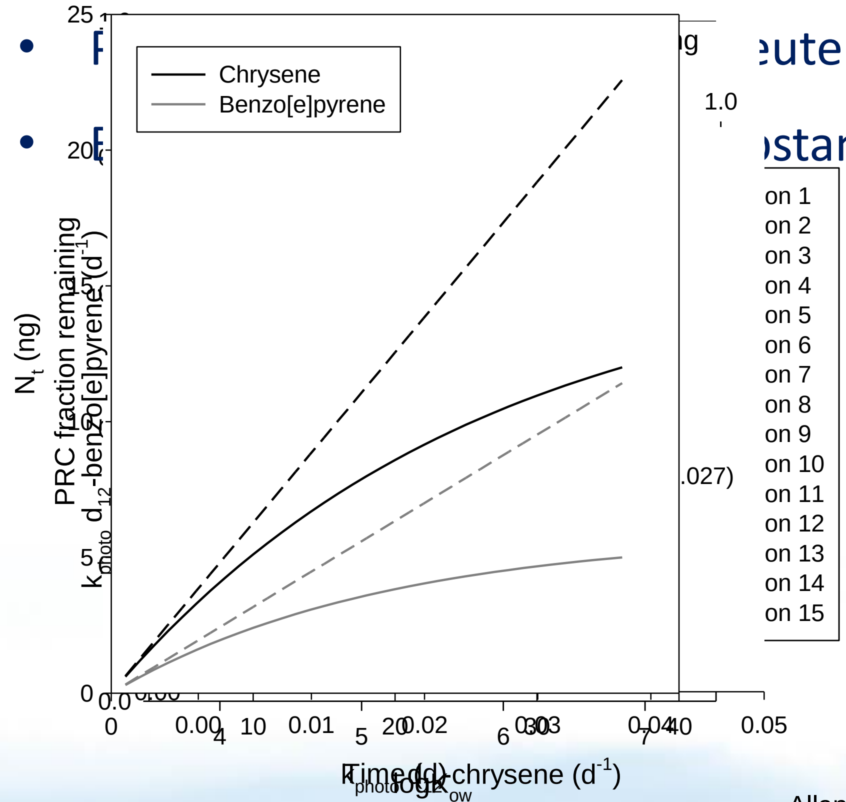
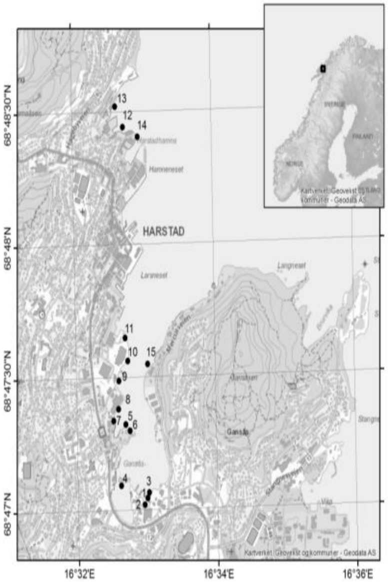
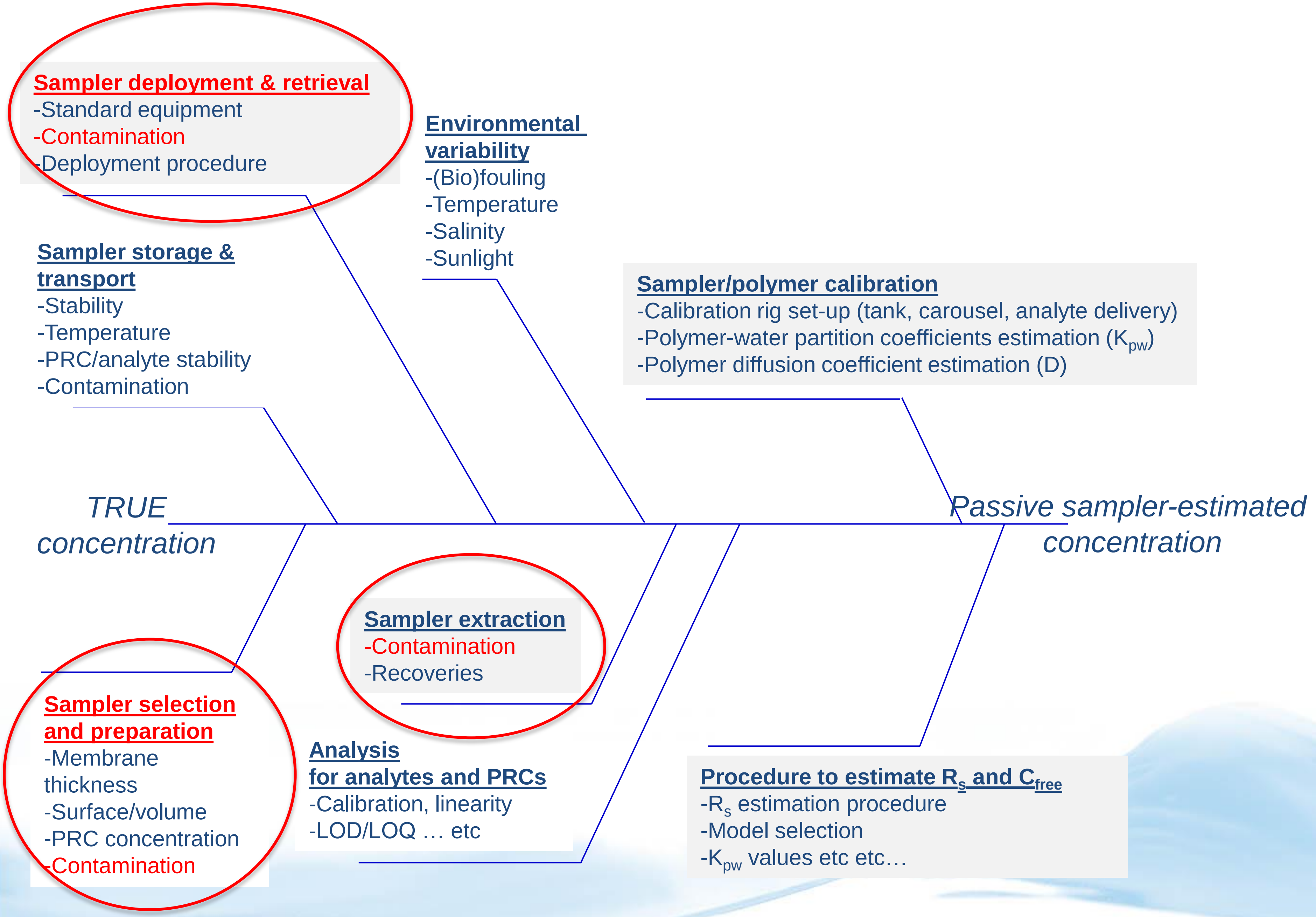
Effect of environmental conditions: Photodegradation

- Semipermeable membrane devices (SPMDs)
- Exposure for 36 days in May at 15 locations in Harstad
- Performance Reference Compounds: Deuterated PAHs
- F … euterated PAH PRCs
- E … ostances being sampled





Allan, I. J., Christensen, G., Bæk, K., & Evenset, A. (2016). Photodegradation of PAHs in passive water samplers. Marine Pollution Bulletin, in pess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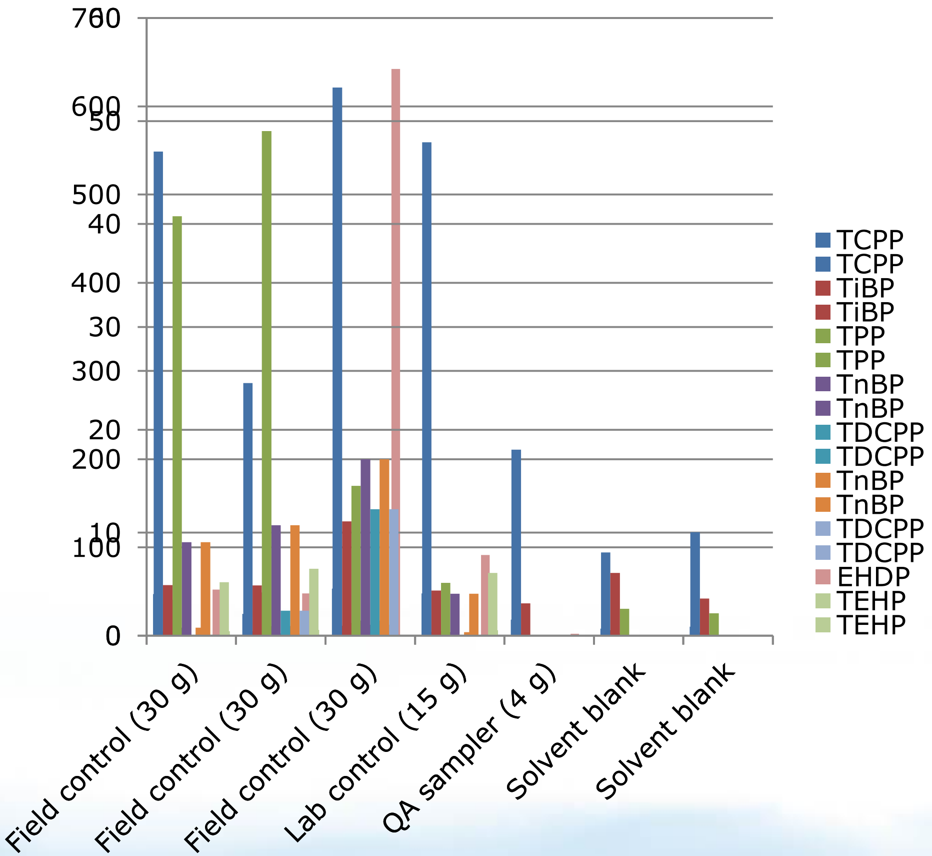
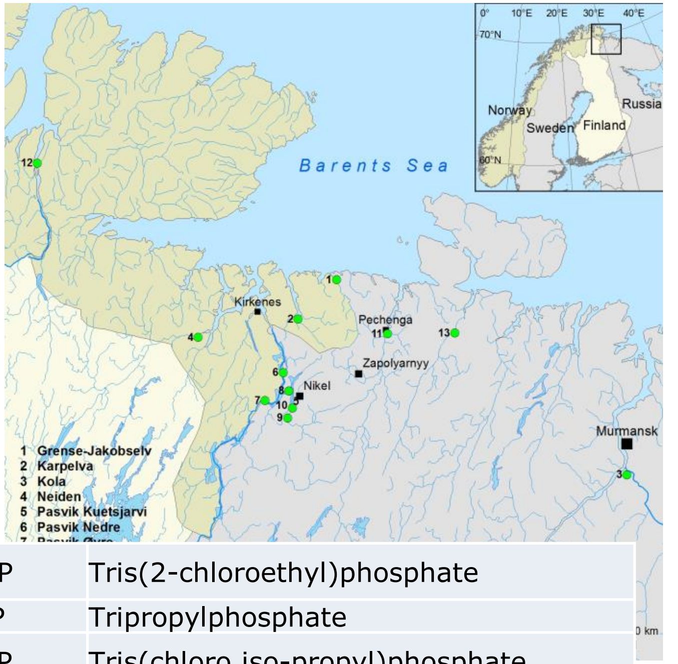
Contamination: Need for blanks

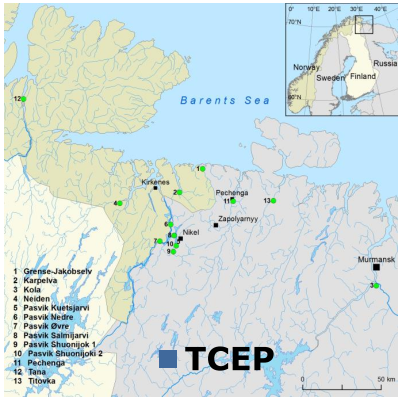
- Silicone rubber samplers (30 g, 1000 cm^2) deployed in Norwegian and Russian Arctic
- OPFRs in QA samplers (ng sampler^{-1})

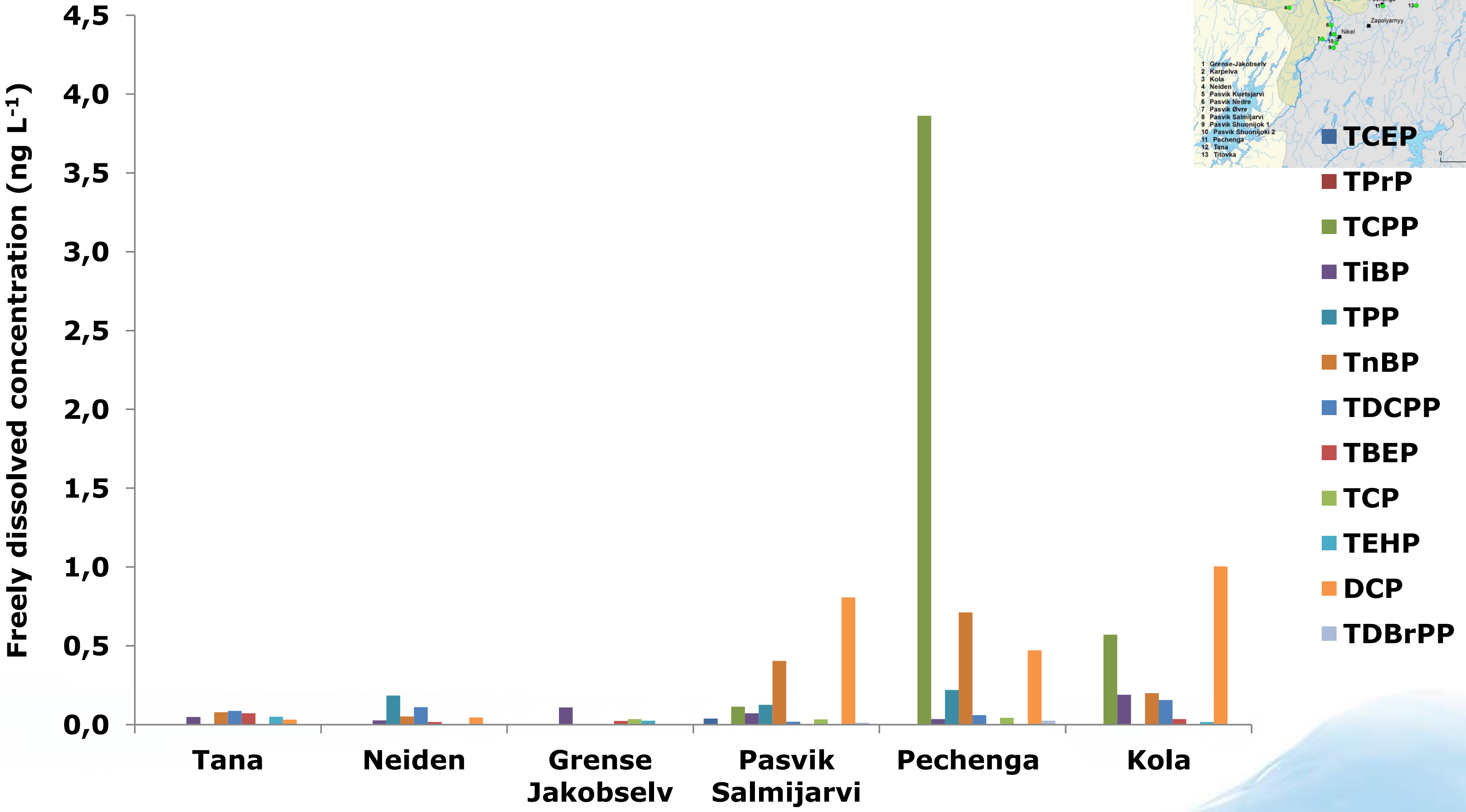


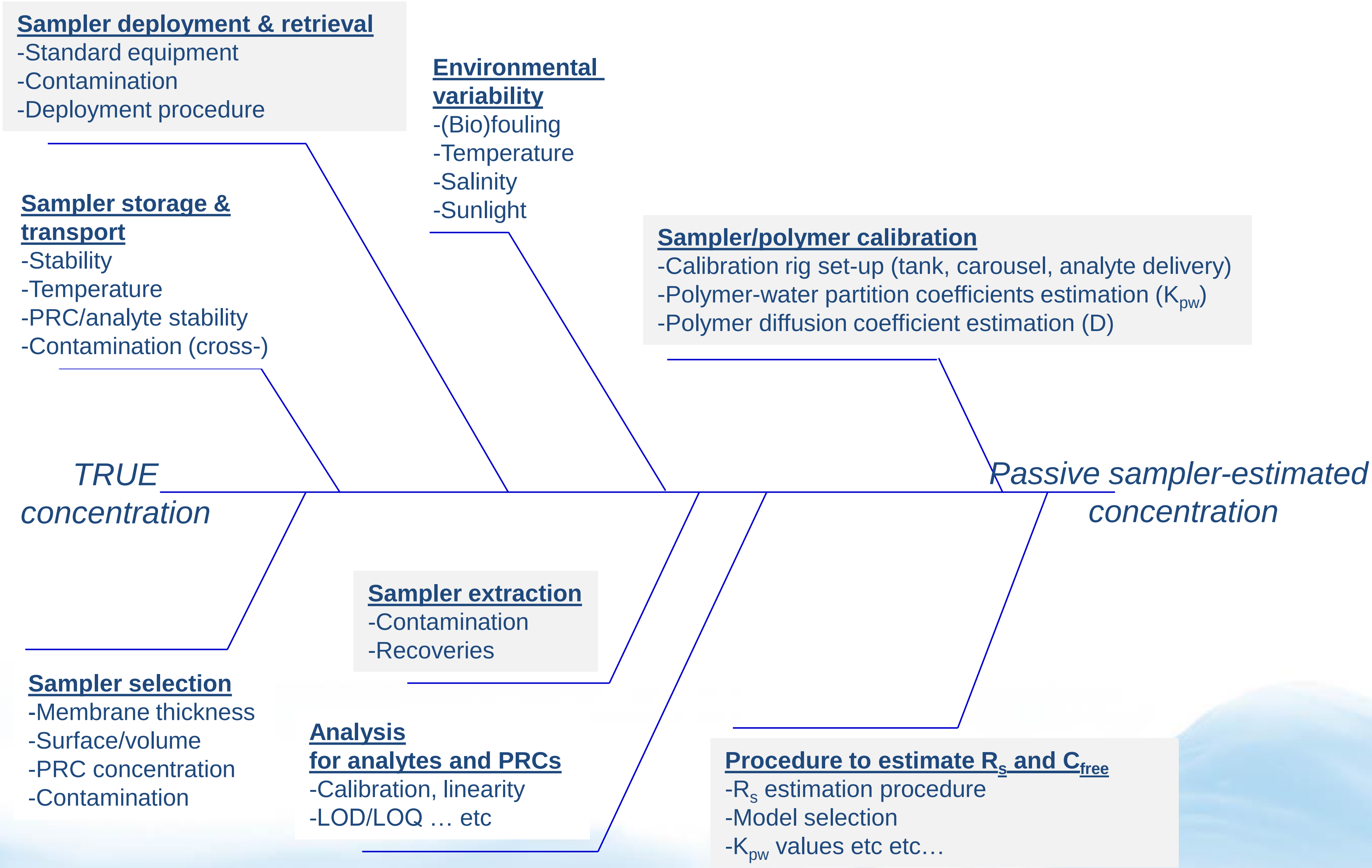


TCEP	Tris(2-chloroethyl)phosphate
TPrP	Tripropylphosphate
TCPP	Tris(chloro iso-propyl)phosphate
TiBP	Tri-iso-butylphosphate
BdPhP	Butyldiphenylphosphate
TPP	Triphenylphosphate
DBPhP	Dibutylphenylphosphate
TnBP	tributylphosphate
TDCPP	Tris(1,3-dichloro-2-propyl)phosphate
TBEP	Tri(2-butoxyethyl)phosphate
TCP	Tricresylphosphate
EHDP	2-ethylhexyl-di-phenylphosphate
TEHP	Tris(2-ethylhexyl)phosphate
DCP	diphenylcresylphosphate
T35DMPP	Tris(3,5-dimethylphenyl) phosphate
TDBrPP	Tris(2,3-dibrompropyl) phosphate

OPFRs in Russian and Norwegian Arctic rivers



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Passive sampling in water, sediment, biota or humans

Where are we now?

	Water	Sediment	Biota	Human
Robustness	***	***	*	*
Validation needs	*	*	***	***
Metadata	***	**	***	*
Info on sampling kinetics	***	**	**	*
Need for blanks	***	***	***	**
Contamination				
-Field manipulation	***	**	**	*
-Lab manipulation	*	***	***	*

* Low

*** High

Passive sampling Cross-Working Group Activity activity for 2016

Objective:

- To develop a common repository for passive sampling data
- To prepare specifications for a module to input passive sampling data into NORMAN's EMPODAT database
- Two teleconference meetings before this summer
- A working meeting this autumn

Concluding remarks

- Specimen banking of PS is feasable
- Can provide a solution to specimen banking of complex matrices
- Robustness of the method: use of blanks and control samplers
- PS has «built-in» selectivity of the chemicals that are sampled and that can be looked for retrospectively
- Requires perhaps more data collection/metadata than the more common specimen bank matrices?
- Needs additional analyses and calculations to estimate environmental concentrations

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