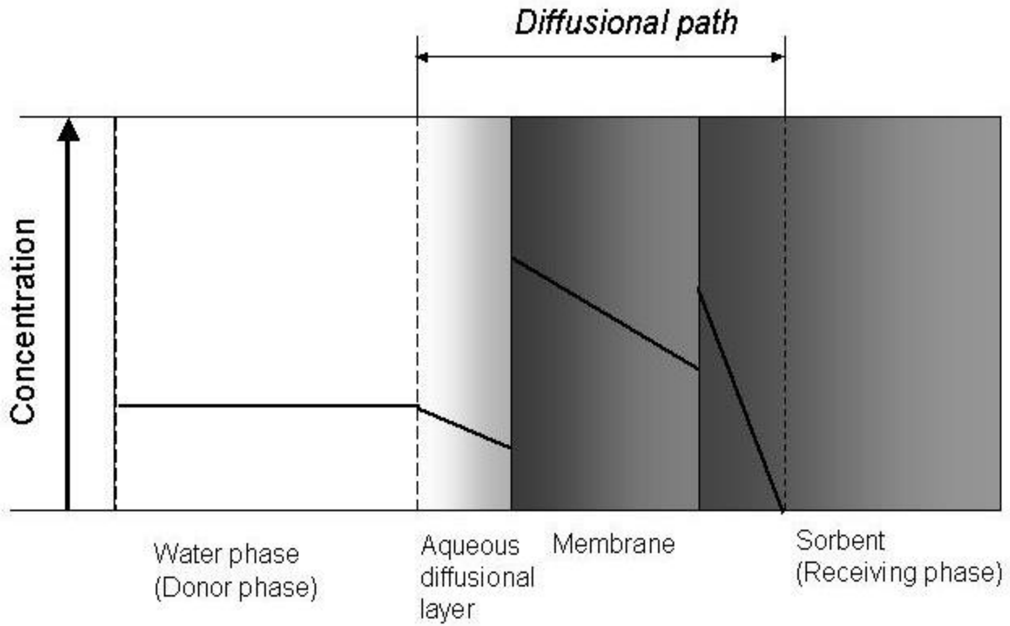
WCMS – Passive sampler application to new compounds

Alkylphenols and naphthenic acids

Ian Allan, Jose Antonio Baz Lomba, Alfhild Kringstad, Saer Samanipour, and Steve Brooks

NIVA

Principle of passive sampling



Sampling to determine time-weighted average concentrations

- A sampler loads analyte in direct proportion to the bulk analyte concentration for the specific sampling period
- Integrative sampling:

$$\int \mathrm{d}C_{\mathrm{s}} \approx \frac{R\mathrm{s}}{V_{\mathrm{s}}} \int C_{\mathrm{w}} \mathrm{d}t = \frac{R\mathrm{s}}{V_{\mathrm{s}}} C_{\mathrm{w,TWA}} \; t$$

The sampling rate, R_S

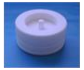
$$C_w = \frac{M_S}{R_S t}$$

The uptake rate, R_S, is influenced by:

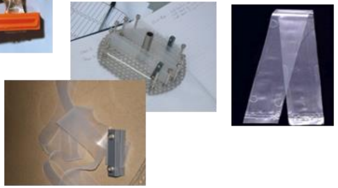
- Temperature
- Turbulences
- Biofouling

Passive sampling operation




Sampler selection

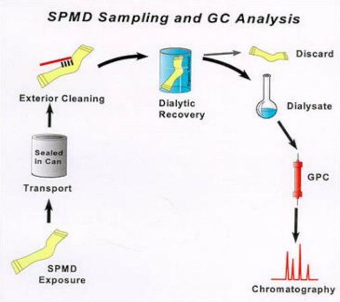


Sampler deployment

Exposure for days-months

Sampler Retrieval

Sampler Extraction and analysis



Modelling...

Calculation of concentration, C_W

Objectives

Develop a passive sampling solution for:

- Alkylphenols

  → Partitioning-based PS with silicone rubber

- Naphthenic acids

  → Adsorption-based PS

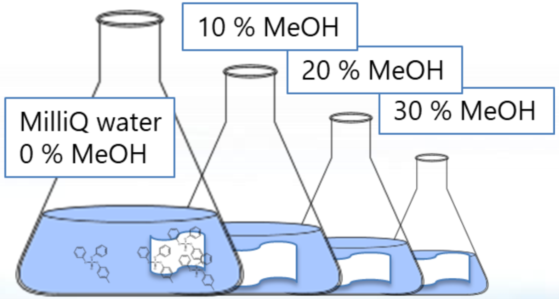
Objectives

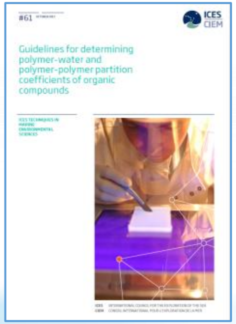
- Calibration of silicone rubber (SSP and AlteSil) for the monitoring of alkylphenols
  - Polymer-water partition coefficient, K_{pw}
- Design and calibration of device for the sampling of naphthenic acids

  Objectives:
  - Minimum dependence of the sampling rate on water turbulences
  - Solution applicable to an as wide range of NAs as possible
  - Applicable to a 6-7 week deployment in the North Sea

SR calibration for alkylphenols

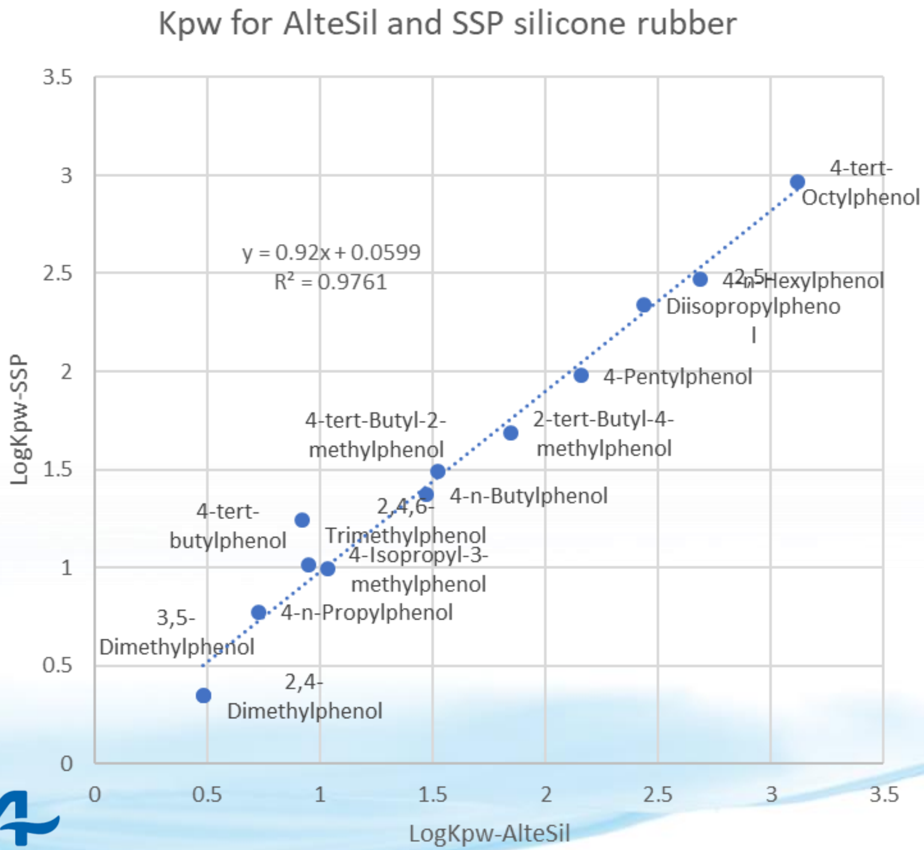
- Selection of 21 alkylphenols
- K_{pw} measurement following guidelines (Booij et al 2017)
  - Use of co-solvent (MeOH) procedure for QA for the most hydrophobic APs

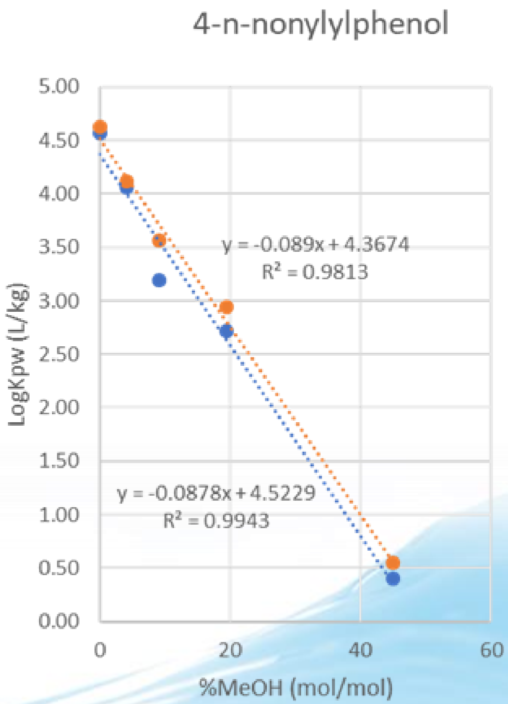




o-Cresol
p-Cresol
2,4-Dimethylphenol
3,5-Dimethylphenol [
4-Ethylphenol
4,6-Trimethylphenol
4-n-Propylphenol
4-n-Butylphenol
4-Isopropyl-3-methylphenol
4-tert-Butylphenol
4-Pentylphenol
2-tert-Butyl-4-methylphenol
4-tert-Butyl-2-methylphenol
4-n-Hexylphenol
2,5-Diisopropylphenol
4-n-Heptylphenol
4-tert-Octylphenol
4-n-Octylphenol
4-n-Nonylphenol
4,6-Di-tert-butyl-2-methylphenol

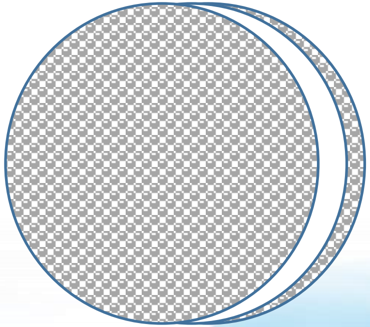
Polymer-water partition coefficients, K_{pw}





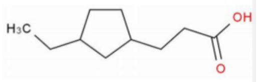
PS sampling for naphthenic acids (NAs)

- HLB SPE disc as receiving phase for the accumulation of naphthenic acids
- Evaluation of thick stainless steel mesh (5 um pore size) as diffusion-limiting membrane



1. Set-up of LC method for model NAs
2. Evaluation of the sorption capacity of HLB discs
3. Membrane calibration

HLB disks: Sorption capacity



Sorbent-water distribution coefficient measurements:

- 24h sorbent-water exposures
- HLB alone
- Two sections of HLB disk
- One section of disk material

	3-Cyclohexyl butanoic Acid	6-Cyclohexyl hexanoic Acid
$\log K_{HLB\text{-}w}$ (L kg^{-1})	5.82	5.89
$\log K_{disk1\text{-}w}$ (L kg^{-1})	4.81	5.26
$\log K_{disk2\text{-}w}$ (L kg^{-1})	5.41	5.61
$\log K_{disk\ material\text{-}w}$ (L kg^{-1})	5.58	5.37

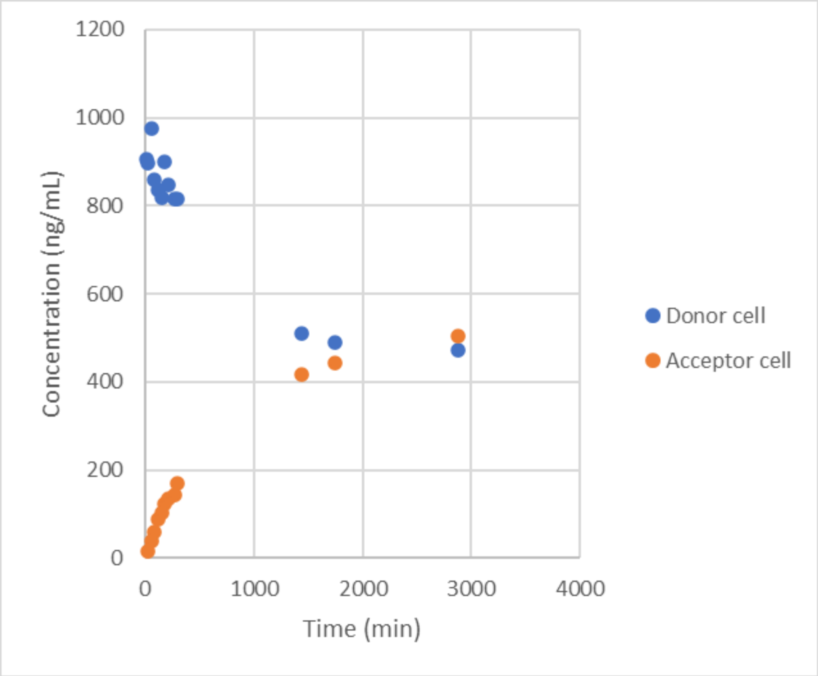
- Preliminary results
- High sorption coefficients

→ High pre-concentration factor
→ Should enable integrative sampling for periods of weeks to months

Membrane calibration: Diffusion cell experiments

- Measure NA diffusion coefficient across a range of membranes:
  - Stainless steel mesh 5 um
  - Stainless steel mesh 10 um
  - Microporous PE?
  - Ceramic?
- On-going…

Transport of 2,2-Dimethyloctanoic acid across the 5um stainless steel mesh

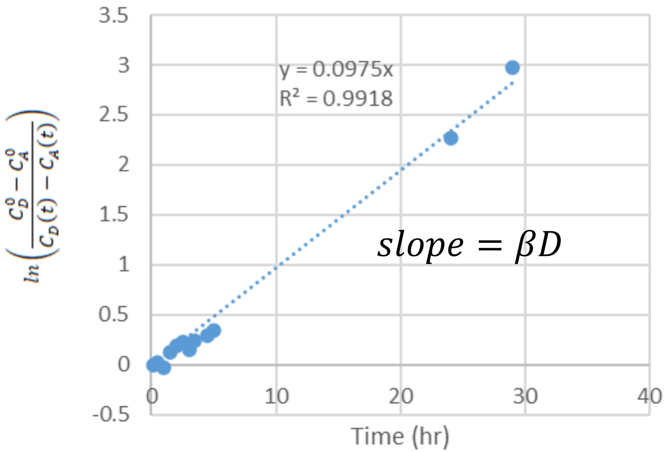


- Minimal sorption of NAs to glass walls
- Functions adequately
- Tested two levels of turbulence → affects boundary layer thickness at membrane surface
- Modelling:

$$D = \frac{1}{\beta t} ln\left(\frac{C_D^0 - C_A^0}{C_D(t) - C_A(t)}\right)$$

$$\beta = \left(\frac{A}{\delta}\right)\left(\frac{1}{V_D} + \frac{1}{V_A}\right)$$

Transport of 2,2-Dimethyloctanoic acid across the 5um stainless steel mesh



Vdon (mL)	125
Vacc (mL)	125
A (cm2)	12.6
Thickness (cm)	0.01
β	20
D (cm2/s)	1.4E-6

D= apparent diffusion coefficient across mesh layer

$R_s = k_0 \, x \, A_{POCIS}$
$= 0.48$ L/d

Still need to evaluate the influence of

- boundary layer
- Resistance in the HLB disc

Work plan – Naphthenic acids

- Repeat the NA-HLB disc sorption experiment
- Continue with the diffusion cell measurements
  - Test different levels of turbulences, vary water temperature and salinity
  - Test other membranes (agarose gel, microporous PE)
- Expected mass transfer limitation in the disc
  - Conducting a more standard calibration?
- Quantification of NAs
  - Target analysis of selected NAs
  - Full scan LC-qTOF
  - Use of technical NA mix and PW for quantification