

Passive sampling for contaminant monitoring

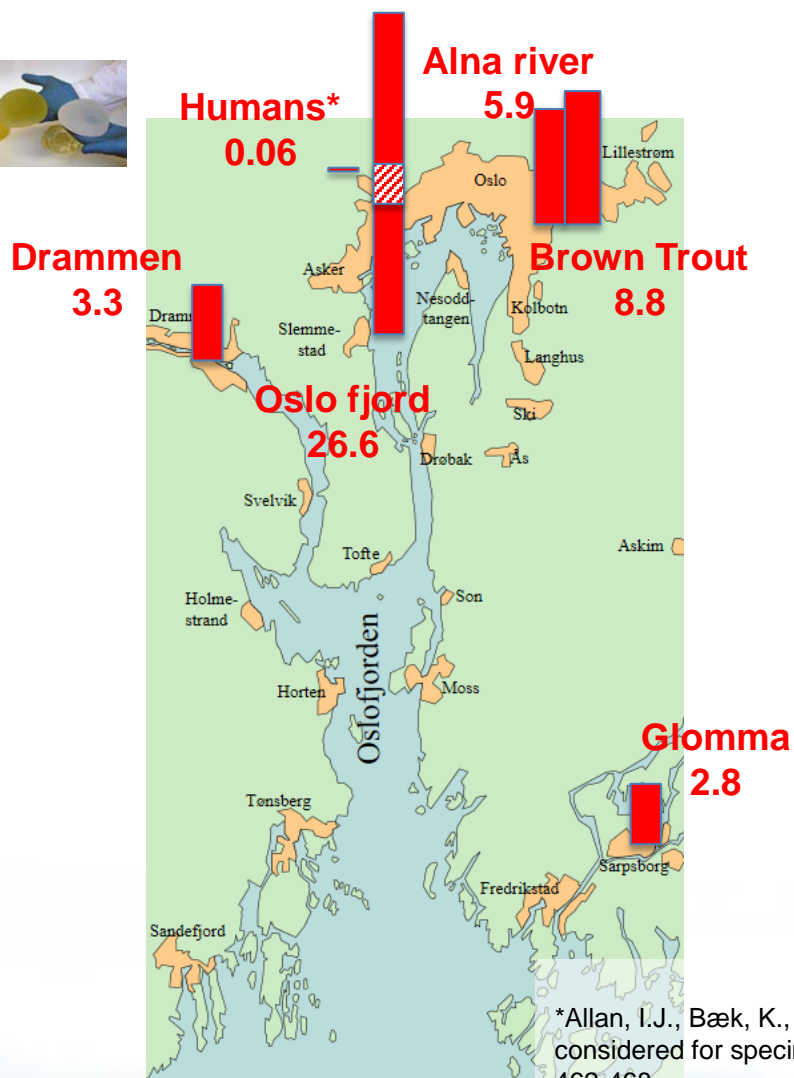
Ian Allan



Passive sampling

- For integrative and/or equilibrium sampling
- Applicable to sampling in air, biota, sediments and water
- Data can be expressed as:
 - C_{free} (ng L⁻¹)
 - $C_{\text{pol, equil}}$ (i.e. ng g⁻¹ silicone rubber)
 - $C_{\text{lip, equiv}}$ (i.e. ng g⁻¹ lipid)
- At equilibrium, concentrations measured in the polymer are proportional to the activity/fugacity of the chemical in the medium being sampled
- Use of performance reference compounds (PRCs) to estimate contaminant exchange kinetics between the sampler and medium being sampled

$C_{pol, equil}$ for CB28 ($ng\ g^{-1}$ sil rubber)



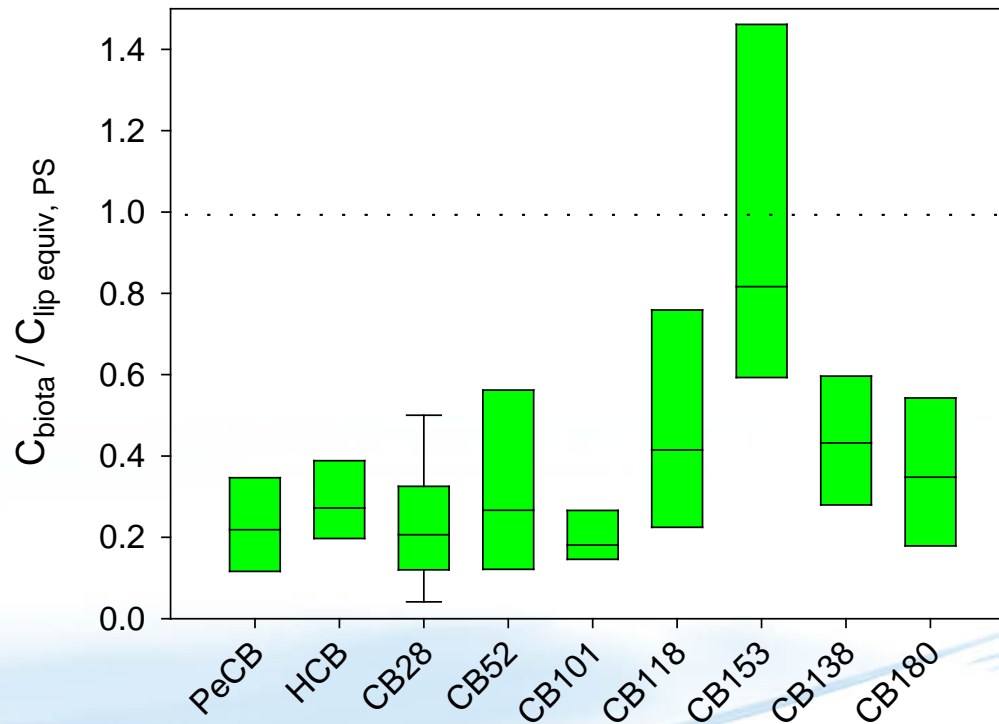
*Allan, I.J., Bæk, K., Kringstad, A., Roald, H.E., Thomas, K.V., 2013. Should silicone prostheses be considered for specimen banking? A pilot study into their use for human biomonitoring. *Env Int* vol 59, 462-468.

**Jahnke, A., Mayer, P., Adolfsson-Erici, M., McLachlan, M.S., 2011. Equilibrium sampling of environmental pollutants in fish: Comparison with lipid-normalized concentrations and homogenization effects on chemical activity. *ET&C Vol 30*, 1515-1521. (corrected to an AlteSil silicone basis)

Can passive sampling help to understand bioaccumulation?

- Paired PS-cod data (Milkys/TFP)
- Multiple sites and years (from Oslofjord to Jan Mayen)
- $C_{\text{biota}}/C_{\text{lip-equiv}}$ ratios < 1 in most cases

$$C_{\text{lip,equiv,PS}} = C_{\text{Free}} \times K_{\text{sil-w}} \times K_{\text{lip-sil}}$$



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

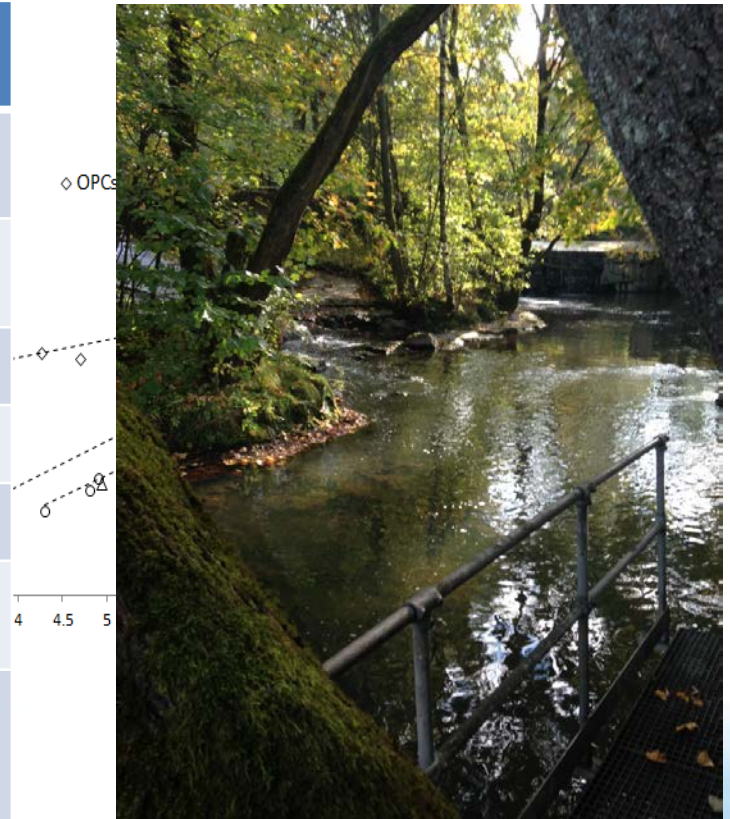
Example of measurement in the River Alna

$\log D_p$

A

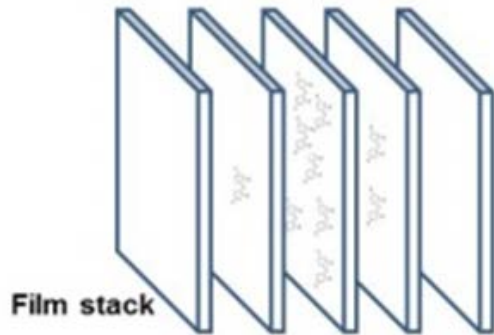
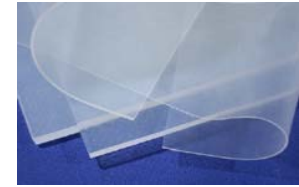
Silicone rubber

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



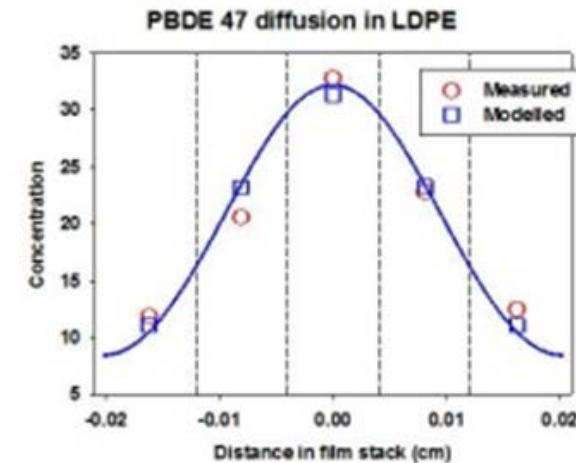
- ▲ Endocrine disruptor compounds
- UV filters
- ◆ Fragrances
- UV filters out-of-range
- OC pesticides (Hale et al. 2010)
- OPCs
- + OPCs lower detection limits

Polymer selection for passive sampling*



- PBDE diffusivities highest in silicone rubber
 - Simplest modelling and estimation of sampling rates

- Low to very low diffusion coefficients in LDPE
 - Relevance of taking into account transport of chemical additives within **microplastic particles** when assessing the risk these pose to aquatic organisms

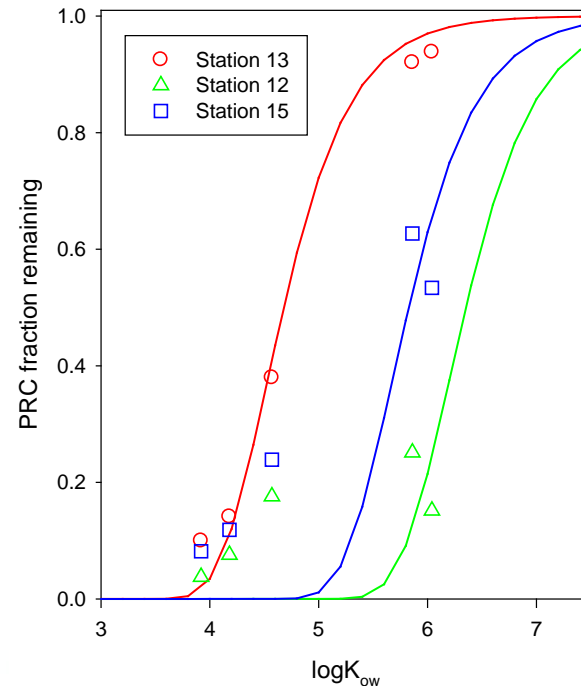


*Narváez Valderrama, Baek, Molina, Allan. Implications of observed PBDE diffusion coefficients in low density polyethylene and silicone rubber. *In press in ESPI*, 2016

Effect of environmental conditions: Photodegradation in SPMDs



- SPMDs deployed for 36 days in the sea around Harstad in May-June
- Unconventional losses of PRCs (deuterated PAH)
- Related to depth
- Can impact masses absorbed in samplers for photosensitive substances



Allan, Christensen, Bæk and Evenset. Photodegradation of PAHs in passive water samplers, *in press in MPB*, 2016

Passive sampling activity of the NORMAN association

- NIVA lead of PS activity (2015-)
- Report of the Joint Danube Survey 3 (2013-2015)
 - Active-passive sampling along the entire Danube river
- Position paper: outcome of workshop in Lyon (Fr)
- Proposed activity for 2016
 - Development of a module to input PS data into the NORMAN database



Position paper on passive sampling techniques for contaminants in the aquatic environment – Ac to date and perspectives

Cécile Miège^{a,*}, Nicolas Mazzella^b, Ian Allan^c, Valeria Dulio^d, Céline Tixier^e, Etienne Vermeirssen^b, Jan Brant^f, Simon O'Tool^g, Jean-Philippe Ghestem^h, Pierre-François Staub^m, Sophie Lardy-Jean-Louis Gonzalez^o, Marina Coquery^a, Branislav Vrana^g

29 Passive sampling: chemical analysis and toxicological profiling

Branislav Vrana, Foppe Smedes, Tatsiana Rusina, Krzysztof Okonski, Ian Allan, Merete Grung, Klára Hilscherová, Jiří Novák, Peter Tarábek, Jaroslav Slobodník

Way forward

- Need for further developments for PS of polar and ionised substances
- Continued development of robust PS calibration data (K_{sw} , D_p , $K_{lip-sil}$)
- Further understand factors that affect contaminant uptake into aquatic organisms
 - Develop long-term paired PS-biota datasets
- Use for screening for new/unknown contaminants