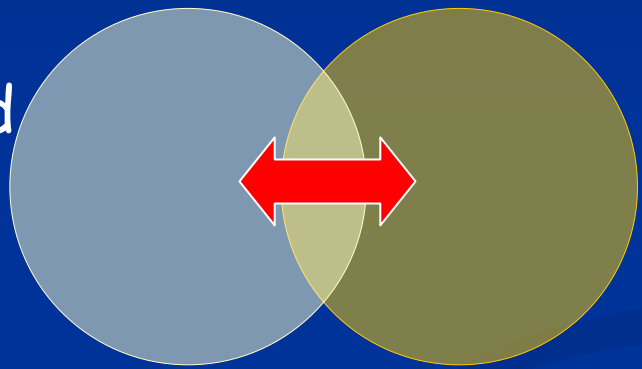
Prioritisation of emerging pollutants – where to focus the future research?

NORMAN expert group meeting

Prague, 27th May 2009

Two areas of research

Technology and methodology development



Technology application

Existing passive sampling techniques

- Sub areas:
  - hydrophobic organic compounds, e.g. POPs
  - polar (hydrophilic) organic compounds such as pharmaceuticals, polar pesticides and illicit drugs
  - trace metals and organometallic compounds

Differences in sampling principles

	Hydrophobic compounds	Polar compounds Metals
Uptake process	Diffusion ➡ Absorption	Diffusion ➡ Adsorption
Driving force	Sampler/water partition coefficient Log K_{SW} ≈ log Kow independent on concentration	Adsorption distribution $K_{SW} \approx Kc^{1/n}$ Adsorption isotherms – dependent on concentration
Speciation	Usually single form sampled	many compounds dissociate multiple pKa - multiple species
Receiving phase selection	Single receiving phase for a broad range of compounds	A range of phases to optimise performance

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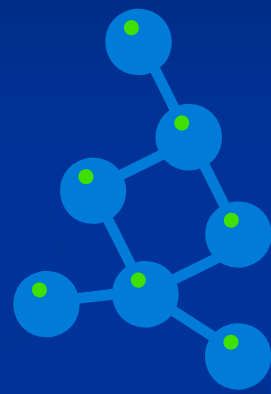
Differences in sampling principles

Most emerging compounds

	Hydrophobic compounds	Polar compounds
Mass transfer	Membrane control log Kow < 3 WBL control log Kow > 3	WBL control For most analytes
Desorption kinetics	Absorption and desorption kinetics are isotropic $K_{e(uptake)} = K_{e(release)}$	Desorption NOT isotropic with adsorption -desorption from multiple binding sites
In situ calibration	Performance reference compounds	PRC use questionable more research needed

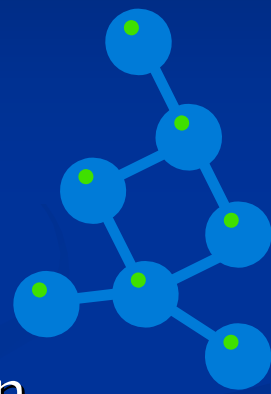
Understanding of principles

- Sorption coefficients
  - Interaction of sampled compounds with materials used for sampler construction
  - experimental data needed
  - adsorption/desorption models
  - predictive models – Quantitative Structure Property Relationships (QSPR)



Understanding of principles

- Mass transfer coefficients
  - Applicability of the PRC approach in adsorbent based passive samplers for polar compounds
  - Model the performance of passive sampler in situations where concentrations of pollutants fluctuate



Combination of passive samplers with bioassays

- Detection and subsequent identification of biologically relevant compounds
- Linking chemical with ecotoxicological information - focus and prioritize future research efforts on compounds with the highest hazardous impact
- Assessment of organism exposure

Applications in ecotoxicity assessment

- Use of extracts from passive samplers in bioassays
- development of contact bioassays compatible with passive sampler receiving phases
- Development of TIE schemes for passive samplers
- Development of biomimetic techniques

Calibration of devices

- Evaluation of the effect of many factors needed:
  - Water flow and turbulence
  - Temperature
  - Biofouling
  - Presence of colloids/particulate matter
  - Salinity
  - pH
  - complex mixtures of contaminants

Calibration of devices

- Calibration methods to measure
  - Sampler/water partition coefficients
  - Sampling rates
    - Static exposure design
    - Static renewal design
    - Continuous flow design
    - *In situ* calibration

Novel materials in sampler construction

- Novel types of sorbent materials
  - Ionic liquids
  - Molecularly imprinted polymers
  - Immunoadsorbents
- Membrane materials for selective diffusion of certain species
- Configuration of specific devices to monitor well defined fractions and species

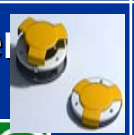
Miniaturisation of devices

- Small devices are less expensive
  - lower cost of material
  - reduced equipment requirements for deployment
  - lower volumes of solvents are consumed
  - easy transportation
  - no depletion of sampled medium
- Disadvantage: sometimes compromised sensitivity

Quality assurance/quality control

- Method validation and PT schemes
- Standards for the use of passive sampling devices

Where to start? Assess performance of available technology

Sampler	Construction	Compounds collected
SPMD 	Semi-permeable membrane devices; flat tube of LDPE filled with triolein	Hydrophobic semivolatile organic compoundswith K_{ow} > 3
Silicone sheets	Sheets of poly(dimethylsiloxane) polymers	Hydrophobic semivolatile organic compoundswith K_{ow} > 3
POCIS 	Solid sorbent material enclosed in a polyethersulphone membrane	Polar pesticides and Pharmaceuticals with log K_{ow} < 3
MESCO 	PDMS rod enclosed in a membrane made of regenerated cellulose or LDPE	Hydrophobic semivolatile organic compounds with log K_{ow} > 3
Ceramic Dosimeter 	Ceramic tube filled with a solid-phase sorbent material, closed with PTFE lids	Groundwater contami-nants with a broad range of physico-chemical properties
DGT 	Two layers of acrylamide gel mounted in a holder device	Metallic elements including the common heavy metals, phospho-rous, sulphide, ^{99}Tc
Chemcatcher 	A housing made of inert plastic, containing a disk of solid sorbent and a disk of diffusion membrane.	Many taylor-made versions; polar and nonpolar organics, metals, organometallic compounds

Performance characteristics of existing technology

- A number of reviews has been published in the last 5 years
- Compilation of data from recently published scientific papers
- Kees Booij prepared an overview (for ICES WGMS) of the established and expected performance of PS's in monitoring priority pollutants
- Söderström compiled POCIS performance characteristics for cca. 50 pharmaceuticals *(J. Chromatogr. A 1216 (2009) 623–630)*

Performance characteristics of existing technology

POCIS performance characteristics for cca. 50 pharmaceuticals

Analyte	Quiscent (Q) R_S (L day^{-1})	Flowing (F) R_S (L day^{-1})	Exp. Q/F[a] (days)	Temp. Q/F[b] (°C)	Ref.
Amitryptiline	n.t.[d]	1.5[e]/2.5[f]	7,14,21	15/21	[39]
Atenolol	0.037	0.040	29/25	22/28	[41]
Azithromycin	0.021	0.120	7,14,28,56	23/27	[32]
Caffeine	n.d.	n.d.	29/25	22/28	[41]
Caffeine	n.t.	0.5[e]/0.5[f]	7,14,21	15/21	[39]
Carbamazepine	0.112	0.348	29/25	22/28	[41]
Carbamazepine	n.t.	3.5[e]/3.5[f]	7,14,21	15/21	[39]
Celecoxib	0.169	0.669	29/25	22/28	[41]
Clarithromycin	0.090	0.668	29/25	22/28	[41]
Clofibric acid	n.d.	n.d.	29/25	22/28	[41]
Codeine	0.090	0.329	29/25	22/28	[41]
Diazepam	n.t.	1.0[e]/2.0[f]	7,14,21	15/21	[39]
Diclofenac	0.092	0.166	29/25	22/28	[41]
Diclofenac	n.t.	1.0[e]/1.0[f]	7,14,21	15/21	[39]
Doxepine	n.t.	2.5[e]/3.0[f]	7,14,21	15/21	[39]
Erythromycin	0.183	0.911	29/25	22/28	[41]
17β-Estradiol	n.t.	0.037	10	15	[38]
Estrone	n.t.	0.040	10	15	[38]
17α-Ethynylestradiol	n.t.	0.051	10	15	[38]
Fenoprofen	0.167	0.230	29/25	22/28	[41]
Fluoxetine	0.223	1.37	29/25	22/28	[41]
Fluoxetine	0.012	0.086	7,14,28,56	23/27	[32]
Gemfibrozil	0.112	0.192	29/25	22/28	[41]
Gemfibrozil	n.t.	0.5[e]/0.5[f]	7,14,21	15/21	[39]
Hydrochlorothiazide	0.016	0.053	29/25	22/28	[41]
Ibuprofen	n.d.	n.d.	29/25	22/28	[41]
Ibuprofen	n.t.	1.0[e]/1.0[f]	7,14,21	15/21	[39]
Imipramine	n.t.	2.0[e]/3.0[f]	7,14,21	15/21	[39]
Indomethacin	n.d.	n.d.	29/25	22/28	[41]
Ketoprofen	0.083	0.135	29/25	22/28	[41]
Ketoprofen	n.t.	1.0[e]/2.0[f]	7,14,21	15/21	[39]
Levothyroxine	0.009	0.053	7,14,28,56	23/27	[32]
Metformin	n.d.	n.d.	29/25	22/28	[41]
Metoprolol	0.097	0.599	29/25	22/28	[41]
Naproxen	0.083	0.116	29/25	22/28	[41]
Naproxen	n.t.	1.0[e]/1.0[f]	7,14,21	15/21	[39]
Nordiazepam	n.t.	1.0[e]/1.5[f]	7,14,21	15/21	[39]
Omeprazole	n.d.	2.46	29/25	22/28	[41]
Omeprazole	0.007	0.030	7,14,28,56	23/27	[32]
Paracetamol	n.d.[c]	n.d.	29/25	22/28	[41]
Paroxetine	n.d.	0.883	29/25	22/28	[41]
Perindopril	n.d.	n.d.	29/25	22/28	[41]
Propranolol	0.147	0.980	29/25	22/28	[41]
Roxithromycin	0.134	0.723	29/25	22/28	[41]
Sulfadimethoxine	0.021	0.091	29/25	22/28	[41]
Sulfamethazine	0.049	0.114	29/25	22/28	[41]
Sulfamethoxazole	n.d.	n.d.	29/25	22/28	[41]
Sulfapyridine	0.041	0.051	29/25	22/28	[41]
Sulfisoxazole	n.d.	0.536	29/25	22/28	[41]
Temazepam	0.128	0.421	29/25	22/28	[41]
Trimethoprim	0.090	0.360	29/25	22/28	[41]

[a] Days of exposure.
[b] Temperature during experiments.
[c] No data available.
[d] Not tested.
[e] L day^{-1} g^{-1} sorbent, at 15 °C, lower or equal to given value.
[f] L day^{-1} g^{-1} sorbent, at 21 °C, lower or equal to given value.

H. Söderström *J. Chromatogr. A 1216 (2009) 623–630)*

Overview on the expected/potential performance

- List of compounds
- Applicability range - physicochemical properties (log K_{ow})
- Stage of development
  - good and demonstrated performance
  - probably good but not demonstrated
  - sampler is unlikely to perform well
- Detection limits
- Time window over which sampling is integrative
- Strenghts and weaknesses (result uncertainty, ease of operation, cost analysis…)

Application range of passive samplers

- screening for the presence and absence of pollutants
- investigating temporal trends in levels of contaminants
- monitoring spatial contaminant distribution
- tracing point and diffusive pollution sources (e.g. hospital effluent, waste water from drug manufactures, and illegal dumping)
- speciation of contaminants
- assessing pollutant fate and distribution between environmental compartments
- measuring TWA concentrations of pollutants
- biomimetic sampling to estimate worst case organism exposure
- assessing toxicity of bioavailable pollutants in time integrated extracts from passive samplers

Issues addressed

- capabilities and limitations of the various passive samplers in relation to environmental conditions, ease of operation, cost, detection limits, and quality assurance and quality control
- identification of emerging pollutants using PS coupled with ecotoxicity testing/chemical analysis
- quantification of pollutants, and the translation of laboratory calibrations to field deployments
- techniques and materials applicable for sampling "difficult" compounds e.g. labile compounds, surfactants, groups of compounds with a specific toxicological mode of action
- Utility and validity of the passive sampling technologies and methodologies within a regulatory context
- Consensus approach to the normation of passive sampling technology
- agreement on an interlaboratory calibration study

Pharmaceuticals, personal-care products, and other emerging polar pollutants of concern measured in rivers and treated sewage effluent streams in Europe and the USA using the Polar Organic Chemical Integrative Sampler (POCIS) (Mills et al. 2007)

Pharmaceuticals	Polar pesticides
Acetaminophen	Alachlor
Azithromycin	Atrazine (and other triazines)
Carbamazepine	Chlorpyrifos
Dephenhydramine	Desethylatrazine and desisopropylatrazine
Propranolol	Diazinon
Sulfa drugs (antibiotics)	Dichlorvos
Tetracycline antibiotics	Diuron
Thiabendazole	Isoproturon
	Metolachlor
Illicit drugs	
Methamphetamine	*Various personal care and industrial products and degradation products*
MDMA	Alkyl phenols (octyl and nonyl phenols)
Natural and synthetic hormones	Benzophenone
17β-estradiol	Caffeine
17α-ethynylestradiol	Cotinine
Estrone	DEET (*N,N*-diethyl-3-methylbenzamide)
Estriol	Indole
	Triclosan
Fire Retardants	Triethyl citrate
Fryol CEF	*Plasticizers*
Fryol FR2	Diethylhexyl phthalate
Tri(2-butoxyethyl)phosphate	Triphenyl phosphate
Fragrances	
3-Methyl-1H-indole	Urobilin (faecal contamination marker)
Indole	
Methyl salicylate	
Tonalide	
HHCB (1,3,4,6,7,8-hexahydro-5,6,6,7,8,8-hexamethylcyclopenta-gamma-2-benzopyran and related isomers)	