An interlaboratory calibration study

NORMAN expert group meeting

Prague, 27th May 2009

An interlaboratory calibration study

- It is important to demonstrate the reliability of the technology to the scientific community, environment and health agencies and public authorities managing chemical contaminants
- Prior to implementation in international monitoring programmes technical guidelines for monitoring should be available and analytical methods should have been tested in different laboratories
- Intercomparison schemes should be in place
- Interlaboratory proficiency tests are required for a full method validation
- Participation to proficiency tests (laboratory evaluating interlaboratory tests) is considered mandatory for laboratories accredited according to ISO 17025 and EN 45003.

Decisions and agreement needed

DEFINE OBJECTIVES

Compounds

Sampled medium

Sampling techniques

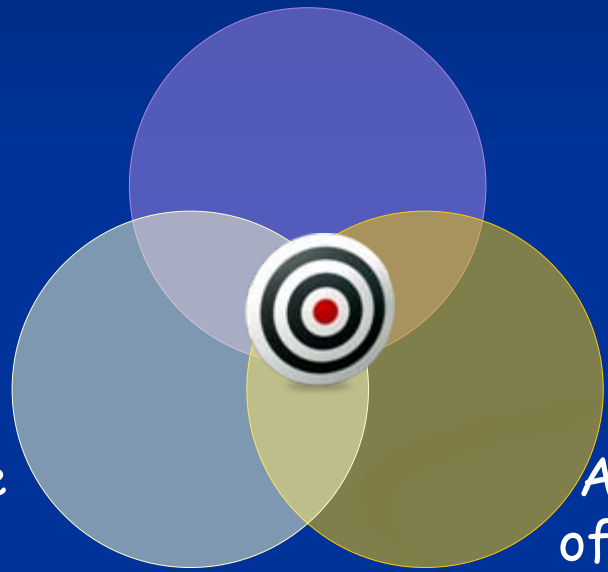
Central expert laboratory

Study setup

Interested participants

A key to a successful intercalibration

Relevant compound group



Mature passive sampling technology

Available methods of chemical analysis or bioassays

Objectives of intercalibration

- extend the validation of the use of passive samplers for monitoring emerging substances in water
- transfer knowledge of the methods more widely within the NORMAN community and beyond
- to gain experience in the use of passive samplers
- estimate the contribution of the analytical component to total variability
- to contribute to mapping of the occurrence of emerging substances in Europe
- to compare the results of the spot sampling of water with the results obtained by passive sampling – may be difficult in some cases
- to assess the possibility of using this tool for compliance checking with the WFD

Selection of a compound group

- The most important decision
  - must be an emerging pollutant group (no priority compounds but can be candidates)
  - sufficient evidence of environmental hazard
  - occurrence in freshwater environment
  - presence identified/expected Europe-wide (or global)
  - might be troublesome substances for monitoring using conventional "bottle" sampling – a challenge

Selection of compounds – overlap with available analytical methods

- Validated methods for instrumental analysis should be available – „mature emerging pollutants“
- Methods for instrumental analysis should be either:
  - available in the participating laboratories
  - not too challenging to setup in terms of infrastructure, instrumentation, method demands
  - passive sampler calibration data available

Candidate compounds

ANNEX III of the DIRECTIVE 2008/105/EC on EQS in the field of water policy

SUBSTANCES SUBJECT TO REVIEW FOR POSSIBLE IDENTIFICATION AS PRIORITY SUBSTANCES OR PRIORITY HAZARDOUS SUBSTANCES

CAS number	EU number	Name of substance
1066-51-9	--	AMPA
25057-89-0	246-585-8	Bentazon
80-05-7		Bisphenol-A
115-32-2	204-082-0	Dicofol
60-00-4	200-449-4	EDTA
57-12-5		Free cyanide
1071-83-6	213-997-4	Glyphosate
7085-19-0	230-386-8	Mecoprop (MCPP)
81-15-2	201-329-4	Musk xylene
1763-23-1		Perfluorooctane sulphonic acid (PFOS)
124495-18-7	--	Quinoxyfen (5,7-dichloro-4-(p-fluorophenoxy)quinoline)
		Dioxins
		PCB

Candidate compounds under WFD

- EU Member States are currently in the process of identifying the substances that are relevant at river basin level (i.e. pollutants which are likely to cause a large number of water bodies within the river basin district to fail the objective of „good ecological status").
- Possible approach: Compare lists of river basin specific compounds in countries of participating laboratories and find overlaps

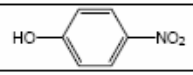
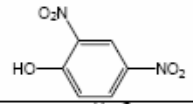
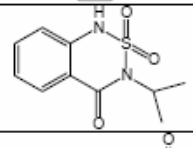
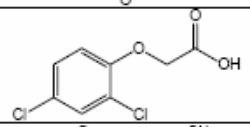
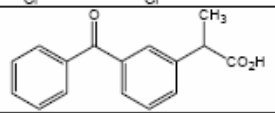
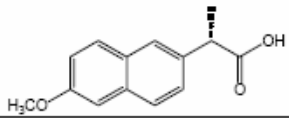
EU Wide Monitoring Survey of Polar Persistent Pollutants (PPP)

- Organised by Joint Research Centre, Institute for Environment and Sustainability
  - European river waters (FATE - EUMORE)
  - groundwater (FATE - GROWS)
  - sewage sludges and effluents (FATE - SEES) in preparation
  - compost (FATE – COMES) in preparation
- FATE – EUMORE
  - 122 individual water samples
  - 100 European rivers, streams or similar water bodies from
  - 27 European Countries
  - 35 selected compounds

FATE – EUMORE compounds

- Perfluorinated compounds
- Pharmaceuticals
- Pesticides
- Industrial chemicals (nitrophenols, benzotriazoles)
- Endocrine disrupting compounds (EDC)

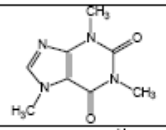
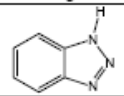
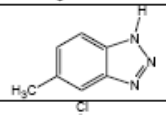
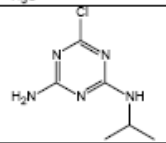
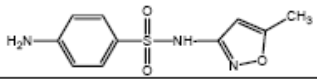
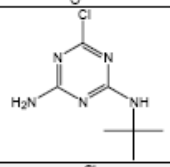
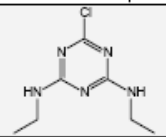
FATE – EUMORE compounds

Chemical	CAS No.	Structure	Comment	Reference
Negative mode (method 1)				
4-Nitrophenol	100-02-7		Nitrophenols are biorefractory organic compounds which are mainly used in the production of pesticides, explosives, dyes and plasticizers. They enter the environment via wastewater discharges from industry, motor vehicle emissions and contaminant degradations or atmospheric inputs, and thus they are ubiquitous environmental contaminants	Zhou and Lei, 2006 Sabio et al., 2006
2,4-Dinitrophenol	51-28-5			
Bentazone	25057-89-0		Diazin contact herbicide; low affinity for particulate or organic carbon; log K_{ow} 0.35	URL2
2,4-D (Dichlorophenoxyacetic acid)	94-75-7		One of the most widely used herbicides in the world; aqueous aerobic half-life of ~ 15 days	URL2
Ketoprofen	22071-15-4		NSAID with analgesic and antipyretic effects	Gros et al., 2006 Tixier et al., 2003
Naproxen	22204-53-1		NSAID commonly used for the reduction of moderate to severe pain, fever, and inflammation caused by conditions such as osteoarthritis, rheumatoid arthritis, injury (like fractures), and menstrual cramps	Gros et al., 2006 Joss et al., 2005 Tixier et al., 2003

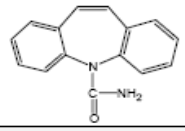
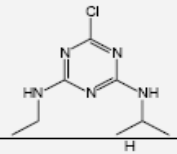
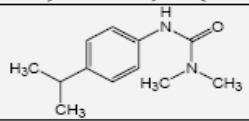
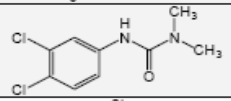
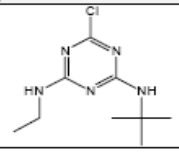
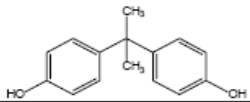
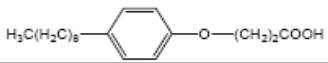
FATE – EUMORE compounds

Bezafibrate	41859-67-0	Fibrate drug used for the treatment of hyperlipidaemia; it helps to lower LDL cholesterol and triglyceride in the blood, and increase HDL	Gros et al., 2006 URL2
Mecoprop	7085-19-0	Hormone-type phenoxy herbicide affecting enzyme activity and plant growth; used on sports turf, for forest site preparation, wheat, barley, and oats, etc.	Blanchoud et al., 2007 URL2
Ibuprofen	15687-27-1	NSAID (analgesic, antipyretic); it is an important non-prescription drug used widely; slowly degraded in aqueous media to hydroxy–and carboxy–ibuprofen	Gros et al., 2006 Joss et al., 2005 Tixier et al., 2003 Winkler et al., 2001
Diclofenac	15307-86-5	NSAID used in human medical care as an analgesic, antiarthritic, antirheumatic compound for reducing pain in conditions such as in arthritis or acute injury	Gros et al., 2006 Joss et al., 2005 Tixier et al., 2003
Gemfibrozil	25812-30-0	Fibrate drug used to lower lipid levels	Gros et al., 2006
Perfluorinated compounds			
PFHxA; perfluorohexanoate	68259-11-0		
PFHpA; perfluoroheptanoate	375-85-9		
PFOA; perfluorooctanoate	335-67-1	The most common use of PFOA is as polymerization aid in the production of fluoropolymers such as polytetrafluoro-ethylene (PTFE), Teflon®, Gore-Tex®; APFO is the ammonium salt of PFOA and the chemical form used in fluoro-polymer manufacturing	URL2
PFNA; perfluorononanoate	375-95-1		
PFOS; perfluorooctansulfonate	EDF-508 Acid: 1763-23-1 NH_4^+:	Surfactant widely used as stain and water repellent in textiles, paper, leather, waxes, polishes, paints, plates, food-containers, bags, cartoons, hydraulic fluid additive,	URL2

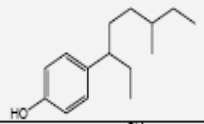
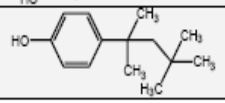
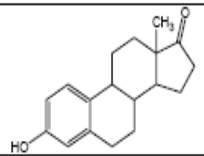
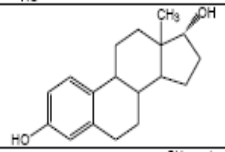
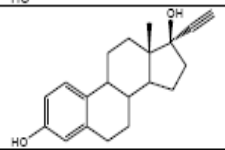
FATE – EUMORE compounds

	29081-56-9		coating additives, or in fire-fighting foams	
PFDA; perfluorodecanoate PFUnA; perfluoroundecanoate	335-76-2 2058-94-8			
Positive mode (method 2)				
Caffeine	58-08-2		Xanthine alkaloid compound that acts as a psychoactive stimulant drug	Moldovan, 2006 URL2
1H-Benzotriazole	95-14-7			
1-Methyl-1H-benzotriazole (Tolyltriazole)	13351-73-0		Anticorrosives used e.g. in dish washers	Weiss and Reemtsma, 2005 Weiss et al., 2006
Atrazine-desethyl	6190-65-4		Persistent metabolite of atrazine	Claver et al., 2006 Planas et al., 2006 Rodriguez-Mozaz et al., 2004b
Sulfamethoxazole	723-46-6		Sulfonamide bacteriostatic antibiotic; relatively persistent in water	Gros et al., 2006 Hu et al., 2007 Joss et al., 2005 Tamtam et al., 2008
Terbutylazine-desethyl	30125-63-4		Persistent metabolite of terbutylazine	
Simazine	122-34-9		Triazine herbicide similar to atrazine	Claver et al., 2006 Noppe et al., 2007 Rodriguez-Mozaz et al., 2004b

FATE – EUMORE compounds

Carbamazepine	298-46-4		Anti-epileptic and mood stabilizing drug; persistent character; it has been proposed due to its stability as a possible anthropogenic marker in the aquatic environment	Andreozzi et al., 2003 Clara et al., 2004 Carballa et al., 2007 Heberer, 2002 Gros et al., 2006 Joss et al., 2005
Atrazine	1912-24-9		Triazine herbicide used globally to stop pre- and post-emergence broadleaf and grassy weeds in major crops; it is one of the most widely used herbicides in the USA, but it has been banned in the EU; quite persistent in water and soil; degradation to dealkylated and hydroxyl metabolites	Blanchoud et al., 2007 Claver et al., 2006 Noppe et al., 2007 Rodriguez-Mozaz et al., 2004b
Isoproturon	34123-59-6		Phenylurea herbicide; mobile in soil; in water, it is quite persistent with a half-life of about 30 days	Claver et al., 2006 Blanchoud et al., 2007 Rodriguez-Mozaz et al., 2004b
Diuron	330-54-1		Phenylurea herbicide; its main use is as anti-fouling agent in boat paints; relative persistent in natural waters	Claver et al., 2006 Rodriguez-Mozaz et al., 2004b
Terbutylazine	5915-41-3		Triazine herbicide which replaces atrazine in the EU; less mobile than atrazine	Claver et al., 2006 Noppe et al., 2007
Phenolic compounds (method 3)				
Bisphenol A	80-05-7		Endocrine disrupting compound (EDC) used in plastic materials (see section 3.5)	Fromme et al., 2002 Céspedes et al., 2006 Loos et al., 2007b Rodriguez-Mozaz et al., 2004b
Nonylphenoxyacetic acid NPE_1C	3115-49-9		Alkylphenol ethoxycaboxylates (APECs) are recalcitrant metabolites of the APEO surfactants; the most prominent species is nonylphenoxyacetic acid (NPE_1C)	Jonkers et al., 2001

FATE – EUMORE compounds

Nonylphenol (NP)	84852-15-3		Alkylphenols are important degradation products of alkylphenol ethoxylates (APEOs) which are nonionic surfactants widely used in agricultural, industrial, and domestic applications; 80 % of the APEO surfactants used are NPEOs, while the remaining 20 % are almost entirely octylphenol isomers (OPEOs)	Céspedes et al., 2006 Loos et al., 2007b
tert-Octylphenol (OP)	140-66-9		Octylphenol has a higher endocrine disrupting potential than NP because it is a single branched isomer	Céspedes et al., 2006 Loos et al., 2007b
Steroid estrogens				
Estrone	53-16-7		Metabolite of estradiol	Gabet et al., 2007 Rodriguez-Mozaz et al., 2004[a],b
17β-Estradiol	50-28-2		Natural hormone	Gabet et al., 2007 Rodriguez-Mozaz et al., 2004[a],b
17α-Ethinylestradiol	57-63-6		Synthetic hormone used in anti-baby pills	Gabet et al., 2007 Rodriguez-Mozaz et al., 2004[a]

Candidate compounds

- Besides the WFD, other programmes are identifying new candidate emerging substances and regularly reviewing their priority lists as scientific knowledge advances:
  - OSPAR
  - HELCOM
  - AMAP
  - BSC
  - UNEP POP

- Kees Booij prepared an overview (for ICES WGMS) of the established and expected performance of PS's in monitoring priority pollutants

Candidate compounds: Calibration data availability

Sampling rates (RS) of pharmaceuticals by polar organic chemical integrative sampler (POCIS) and test parameters used during the experiments

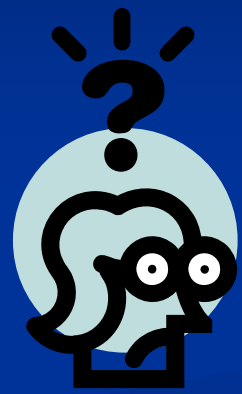
Analyte	Quiscent (Q) R_S (L day^{-1})	Flowing (F) R_S (L day^{-1})	Exp. Q/F[a] (days)	Temp. Q/F[b] (°C)	Ref.
Amitryptiline	n.t.[d]	1.5[e]/2.5[f]	7,14,21	15/21	[39]
Atenolol	0.037	0.040	29/25	22/28	[41]
Azithromycin	0.021	0.120	7,14,28,56	23/27	[32]
Caffeine	n.d.	n.d.	29/25	22/28	[41]
Caffeine	n.t.	0.5[e]/0.5[f]	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.

from H. Söderström et al. / J. Chromatogr. A 1216 (2009) 623–630

Sampled medium

- Drinking water
- Surface water
- Wastewater
- Sediment?



Selection of passive sampling techniques

- Availability of a suitable „mature“ technique in terms of performance criteria
- Agreement needed between research groups using different samplers
- Comparison of a few different samplers for one group of compounds possible in one study, but the number should not be too large – otherwise the number of samples to be processed too high

Selection of passive sampling techniques

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

Selection of passive sampling techniques

- Techniques for sampling hydrophobic organic compounds are most advanced
- Samplers for polar (hydrophilic) organic compounds – under development, sometimes difficulties in data interpretation
- trace metals – well advanced technology
- organometallic compounds – depends on the compound

Problems with PT setup

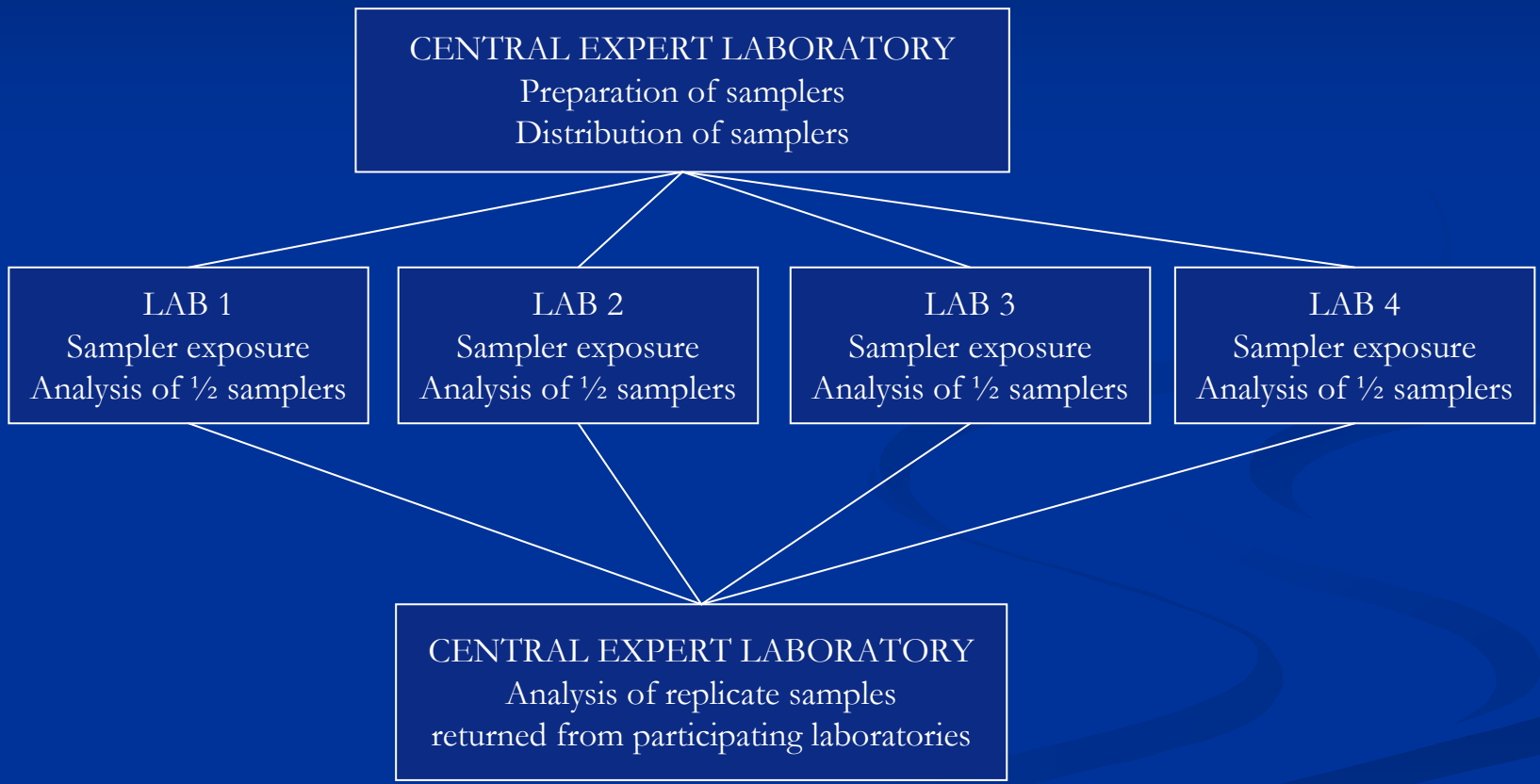
- Laboratory–based proficiency schemes using certified reference materials are not straightforward -large volumes of standard solutions required for calibration procedures
  - use of stable pelletised formulations that can be dispersed under standard conditions to produce large volumes of calibration solutions
  - the use of reference field sites, as have been used for studies of sediments

Previous intercalibration studies

- STAMPS intercalibration of Chemcatcher
- ICES passive sampling trial survey
- IPSIC analytical PT for field exposed SPMD, DGT – recent initiative

Intercalibration setup

Use the approach from the pioneer work of ICES PSTS



Intercalibration setup

Central expert laboratory

Report results

LAB 1
Sampler exposure and analysis

Send a portion of samplers for analysis

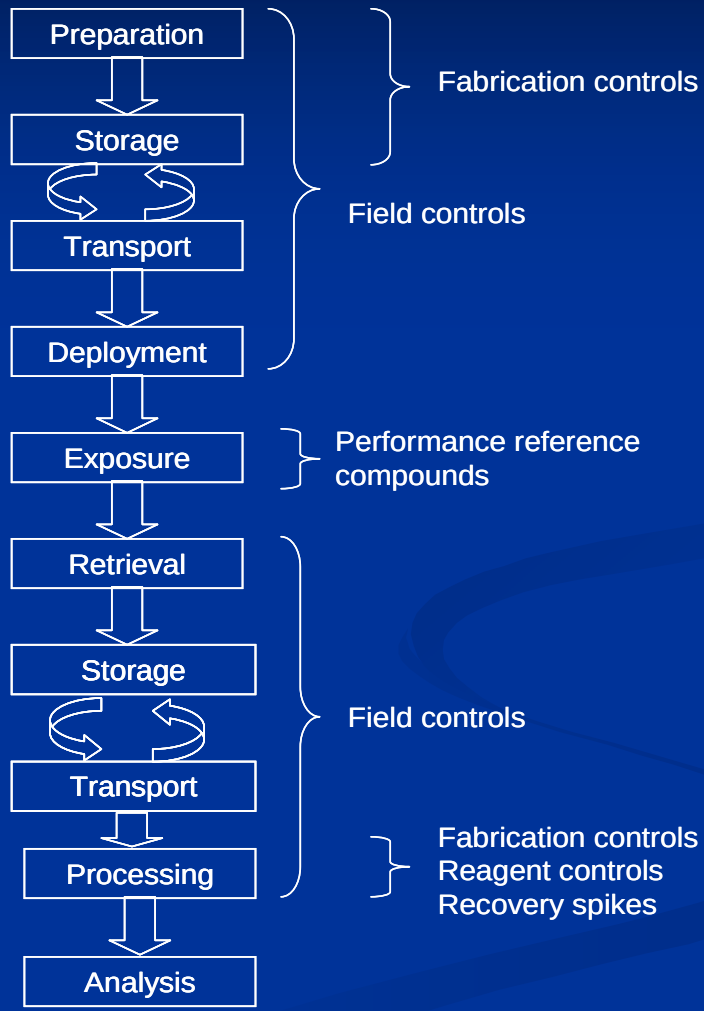
PASSIVE SAMPLING

Comparison

WATER SAMPLING

Adsorption of polar compounds to particles is generally low, which in principle enables comparison

QA/QC


Preparation
Storage
Transport
Deployment
Exposure
Retrieval
Storage
Transport
Processing
Analysis
Fabrication controls
Field controls
Performance reference compounds
Field controls
Fabrication controls
Reagent controls
Recovery spikes

Decisions and agreement needed

DEFINE OBJECTIVES

Compounds

Sampled medium

Sampling techniques

BUDGET

Central expert laboratory

Study setup

Interested participants