Can passive samplers be used for monitoring under the MSFD and WFD?

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marinescotland science

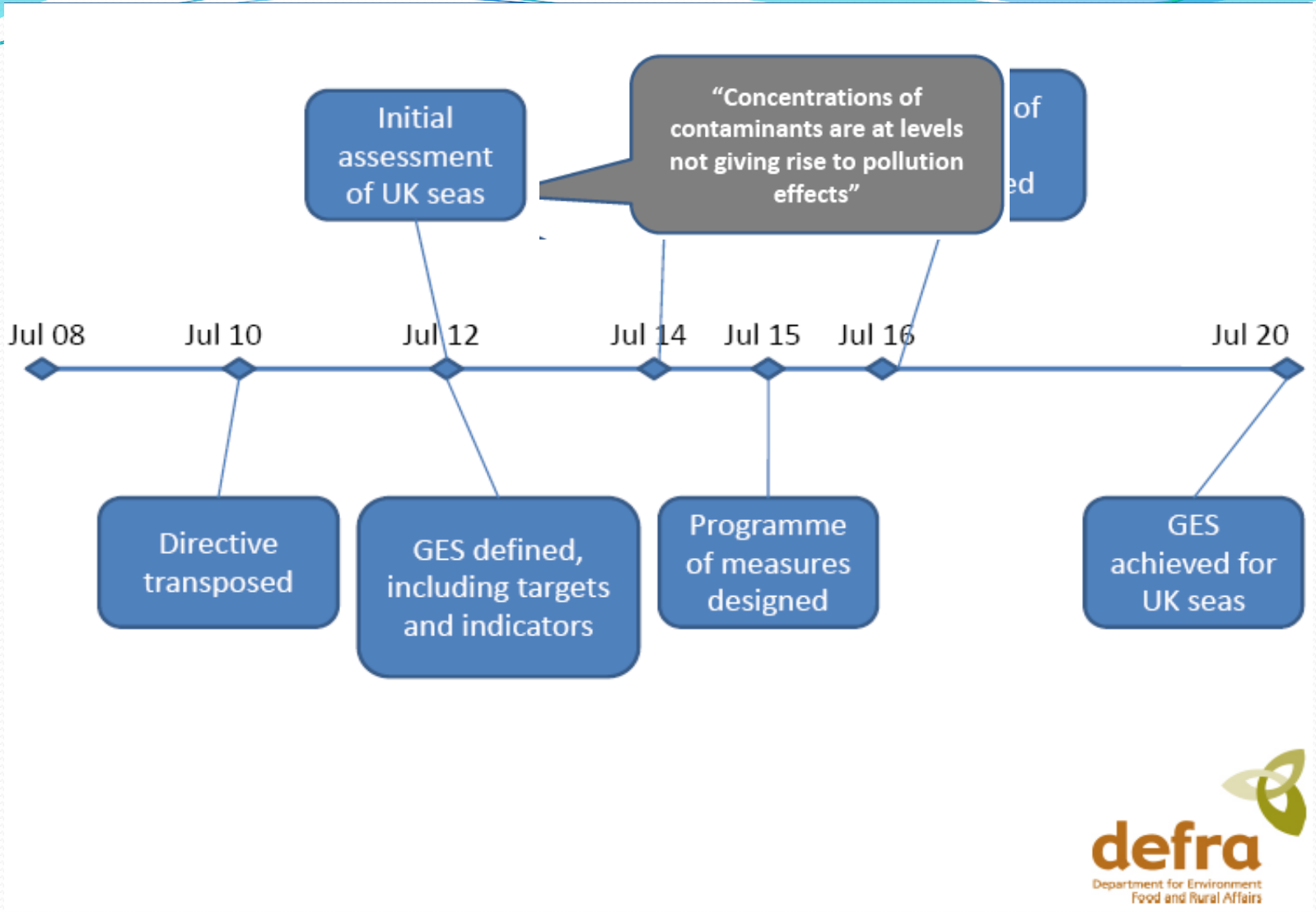
SEPA Scottish Environment Protection Agency

Environment Agency

Deltares Enabling Delta Life

NIEA Northern Ireland Environment Agency www.ni-environment.gov.uk

Cefas



defra
Department for Environment Food and Rural Affairs

Drivers for work

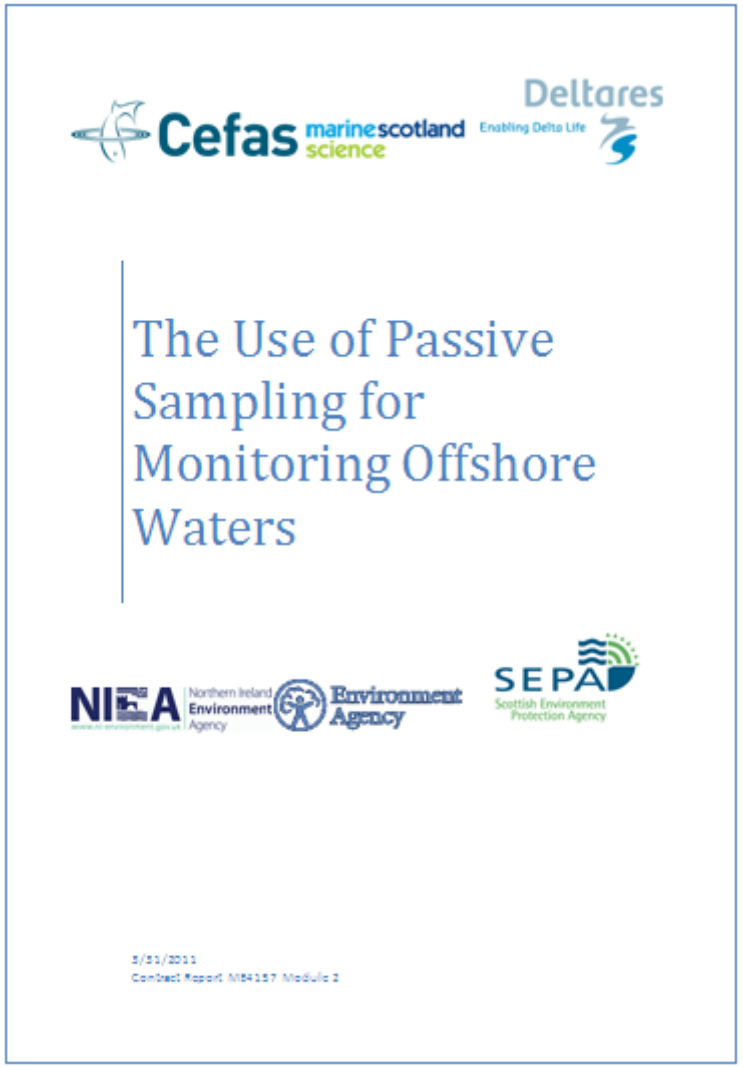
Cefas

Specific Challenges

Cefas

Defra Passive Sampling Survey

- UK wide collaboration
  - Five UK Agencies
    - Centre for Environment, Fisheries and Aquaculture Science
    - Environment agency
    - Marine Scotland
    - Scottish Environmental Protection agency
    - Northern Ireland Environment Agency
  - Deltares (NL)



Aims of the Project

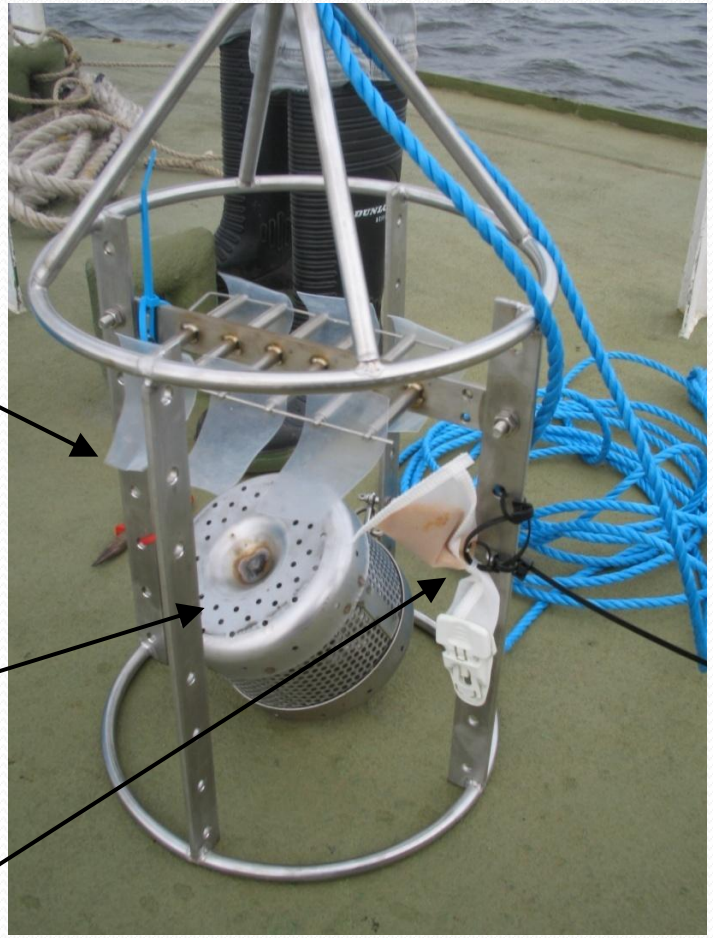
- To create a record of baseline data
  - Important for now and the future
- Source of data for initial assessments
- Current priority substances – are they there?
- A tool to assess future priorities
- Assessment of passive samplers
  - Do they give us additional information?
  - Are they practical?
- Assessment of 'harm'

Cefas

Silicon Rubber
•For Hydrophobic compounds

POCIS
•For hydrophilic compounds

SPATT bags
•Algal Toxins



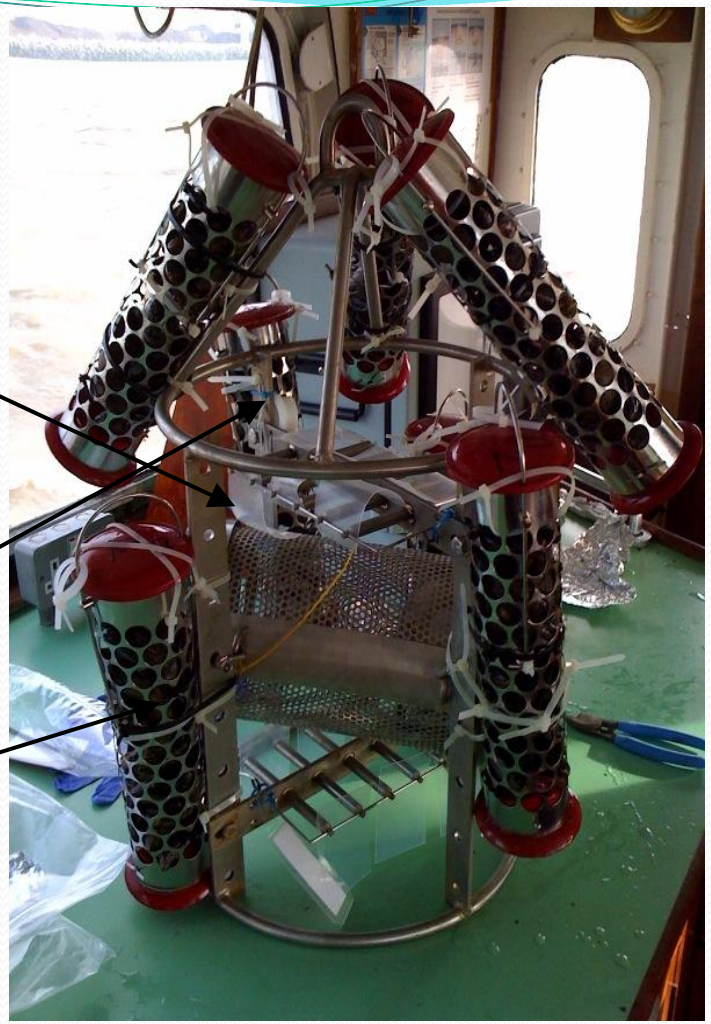
Samplers used

Cefas

Silicon Rubber
•For Hydrophobic compounds

DGT

Mussels



Samplers used Phase 2

Cefas

- Organics
- WFD Priority Substances
- OSPAR Priority Pollutants
- Standard methods where available in UK agency labs
- Where methods unavailable, compounds measured using screening methods

Choice of analytes

Cefas

Group	Hazardous Substance	Cefas	EA	FRS	SEPA	NIEA
Volatile organic compounds	Benzene					✓*
Chlorobenzenes	Pentachlorobenzenes		✓			
	Trichlorobenzenes		✓			
Chlorinated alkanes	Chloroform					✓*
	Dichloromethane					✓*
	1,2-dichloroethane					✓*
Dioxins and furans	PCDDs		✓			
	PCDFs		✓			
Pesticides/biocides	Pentachlorophenol				✓	
	Hexachlorobenzene				✓	
	HCHs				✓	
	Methoxychlor					
	Trifluralin				✓	
	Endosulphan				✓	
	Dicofol					
	HCBD				✓	
	Chlorfenvinphos					
	Alachlor					

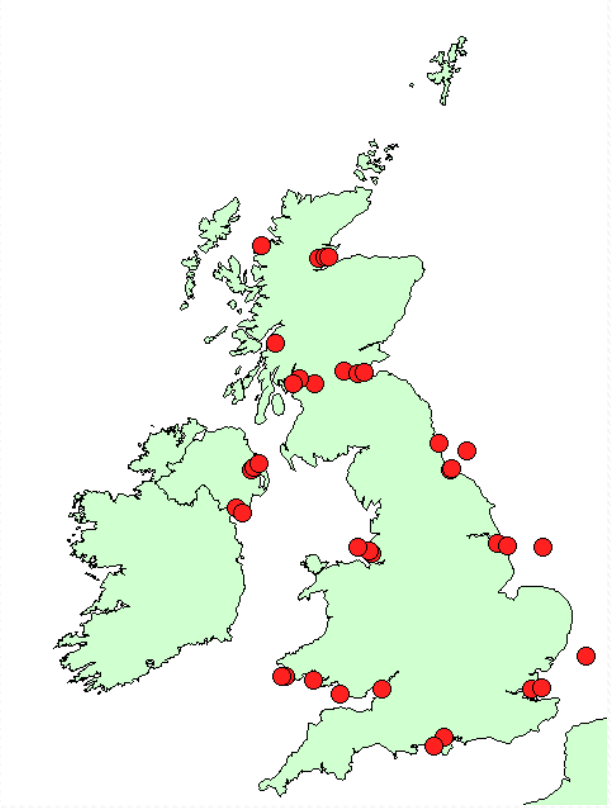
Compounds measured

Cefas

Group	Hazardous Substance	Cefas	EA	FRS	SEPA	NIEA
PCBS	PCBs			✓		
PAHs	PAHs			✓		
Musk xylenes	Musk xylenes		✓			
SCCPs	SCCPs		✓			
Brominated flame retardants	TBBP-A	✓				
	PBDEs	✓				
	HBCD	✓				
Phthalates	DBP & DEHP		✓			
Alkylphenols	Octyl phenols				✓	
	Nonylphenols/ethoxylates				✓	
	2,4,6-tri-*tert*-butylphenol					
Metals and organometals	Organotins	✓				
Pharmaceuticals	Clotrimazole	✓				

Compounds measured

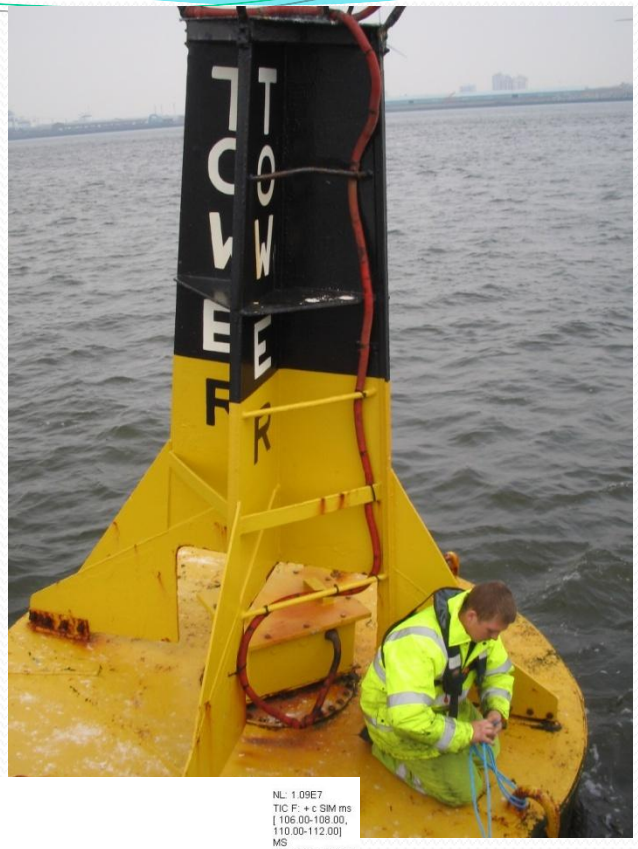
Cefas

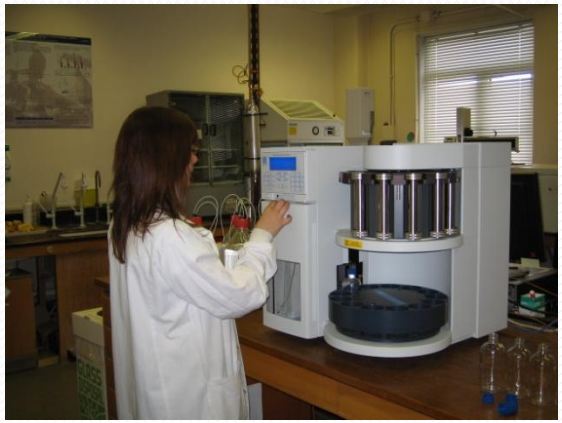


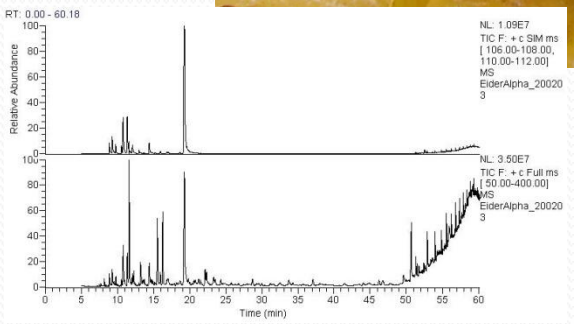
- 38 sites around UK
- Sufficient spatial definiton around UK to be meaningful
- Major contaminant sources captured
- Inputs from land-based, industrial and legacy sources measured
- In shore, near shore and offshore sites considered

Project Plan

Cefas

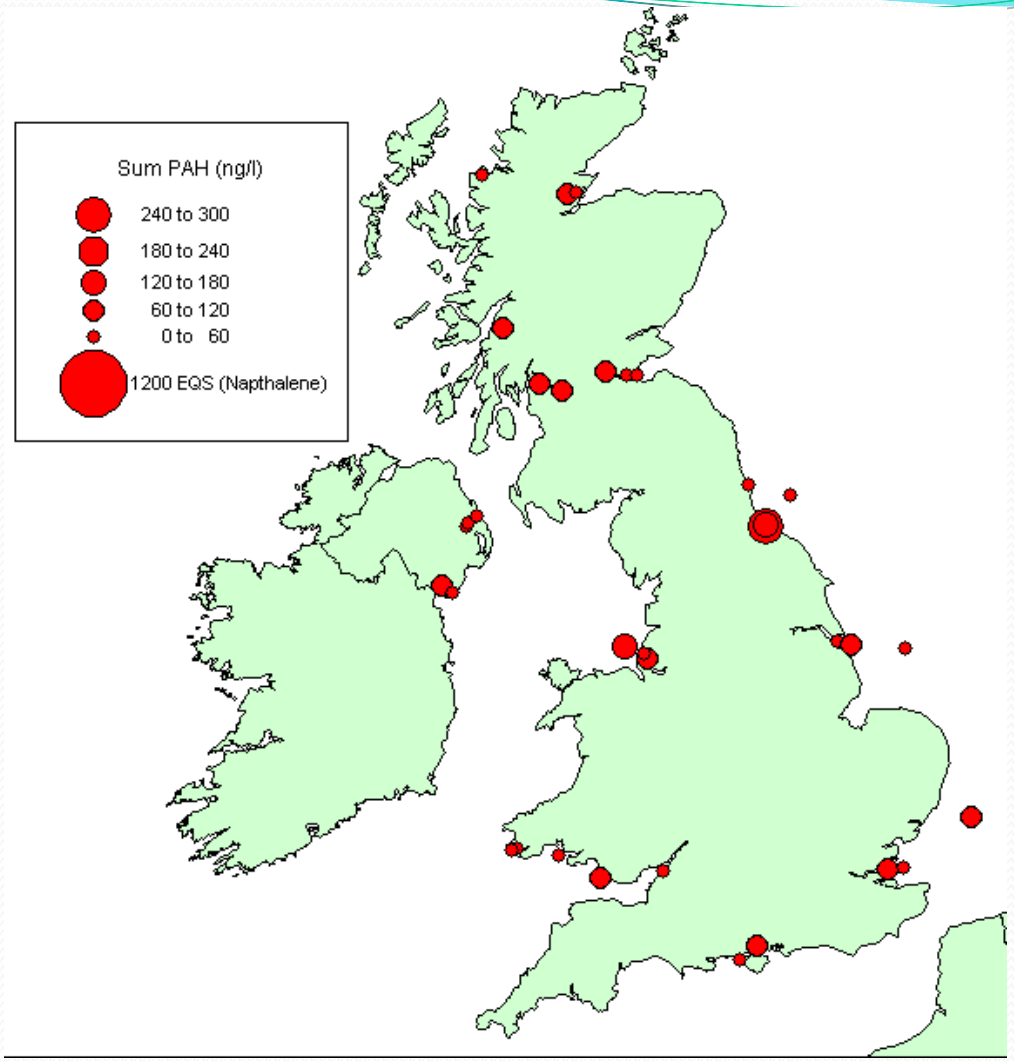






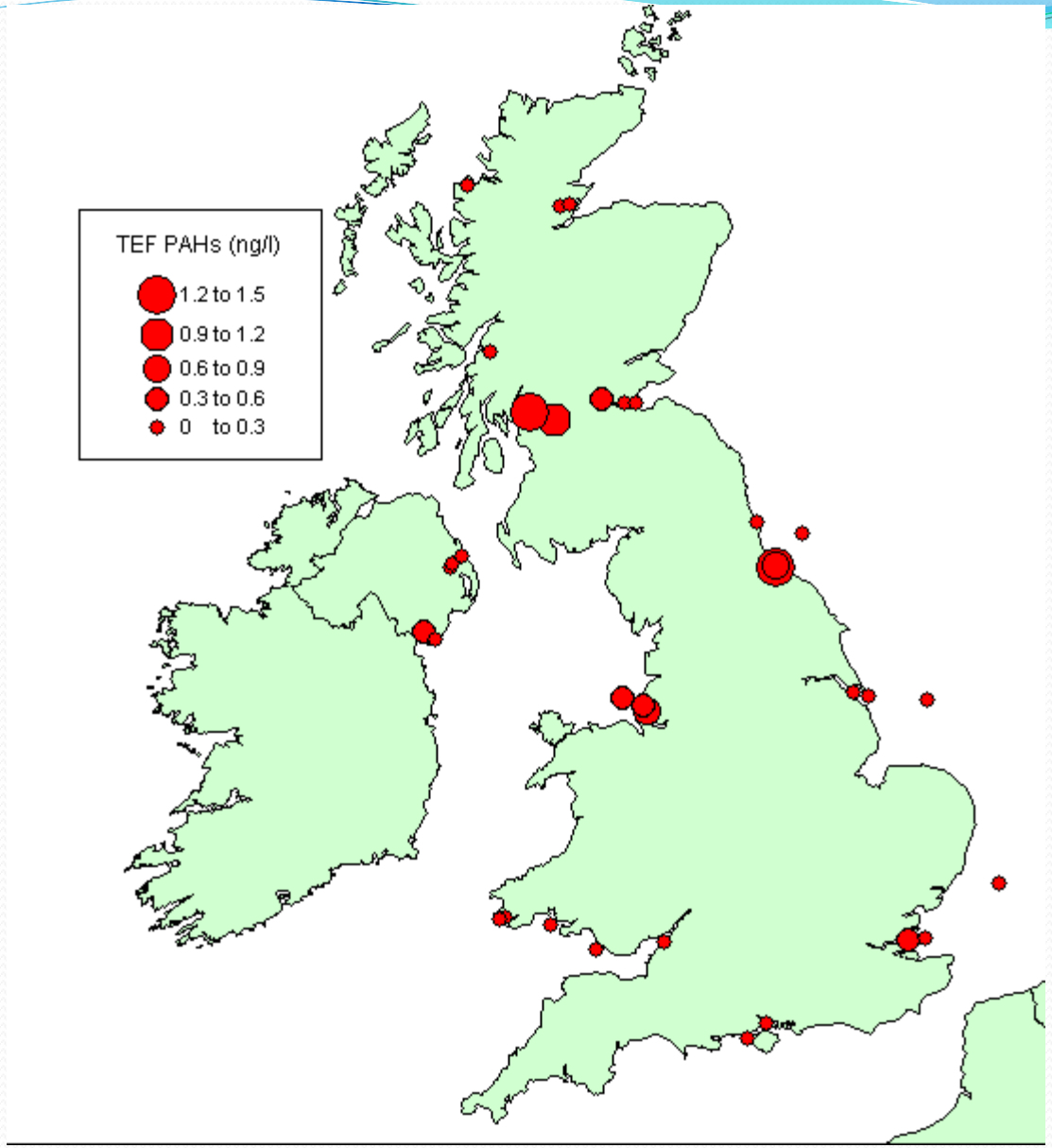
Some Results

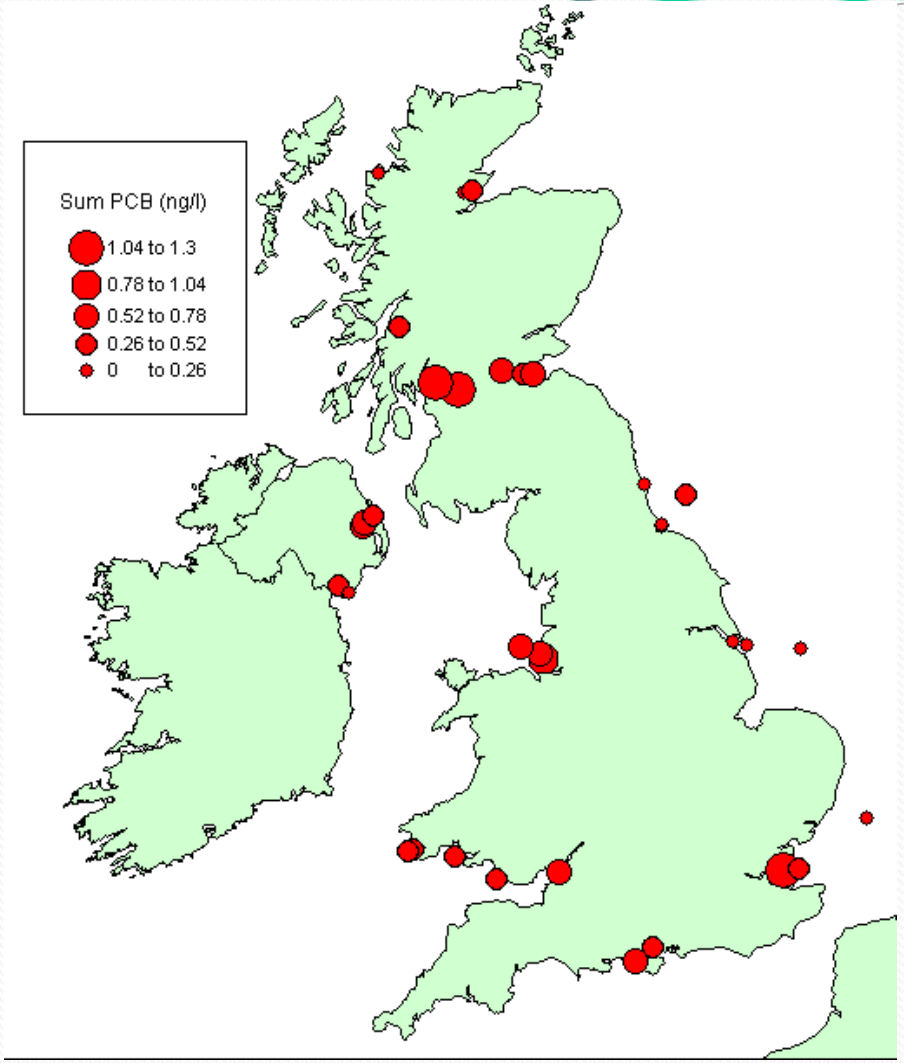
Cefas


Sum PAH (ng/l)
240 to 300
180 to 240
120 to 180
60 to 120
0 to 60
1200 EQS (Napthalene)

PAH

Cefas


TEF PAHs (ng/l)
1.2 to 1.5
0.9 to 1.2
0.6 to 0.9
0.3 to 0.6
0 to 0.3



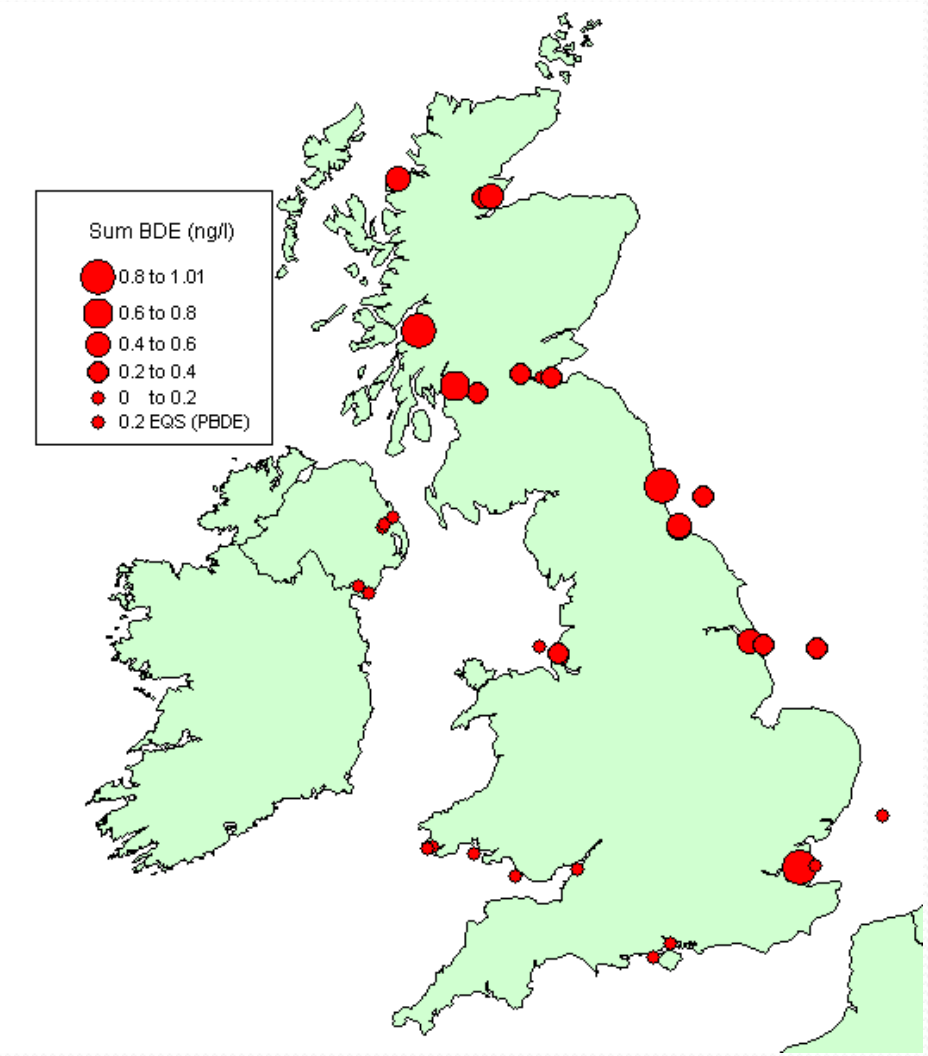
PCB

Cefas

PCB	Morston Baseline	Morston Final	Humber 1	Humber 2	Mersey 2	Mersey 3
CB#28	0.72	0.13	1.5	1.8	1.2	1.4
CB#52	0.64	<0.070	2	2.5	2.1	2.1
CB#101	0.22	<0.070	0.59	0.72	1.8	1.1
CB#118	0.2	0.13	0.41	0.53	1.4	0.94
CB#153	0.64	0.47	0.55	0.66	2.2	1.5
CB#138	0.45	0.37	0.46	0.52	1.9	1.2
CB#180	<0.077	0.073	<0.077	<0.078	0.41	0.2

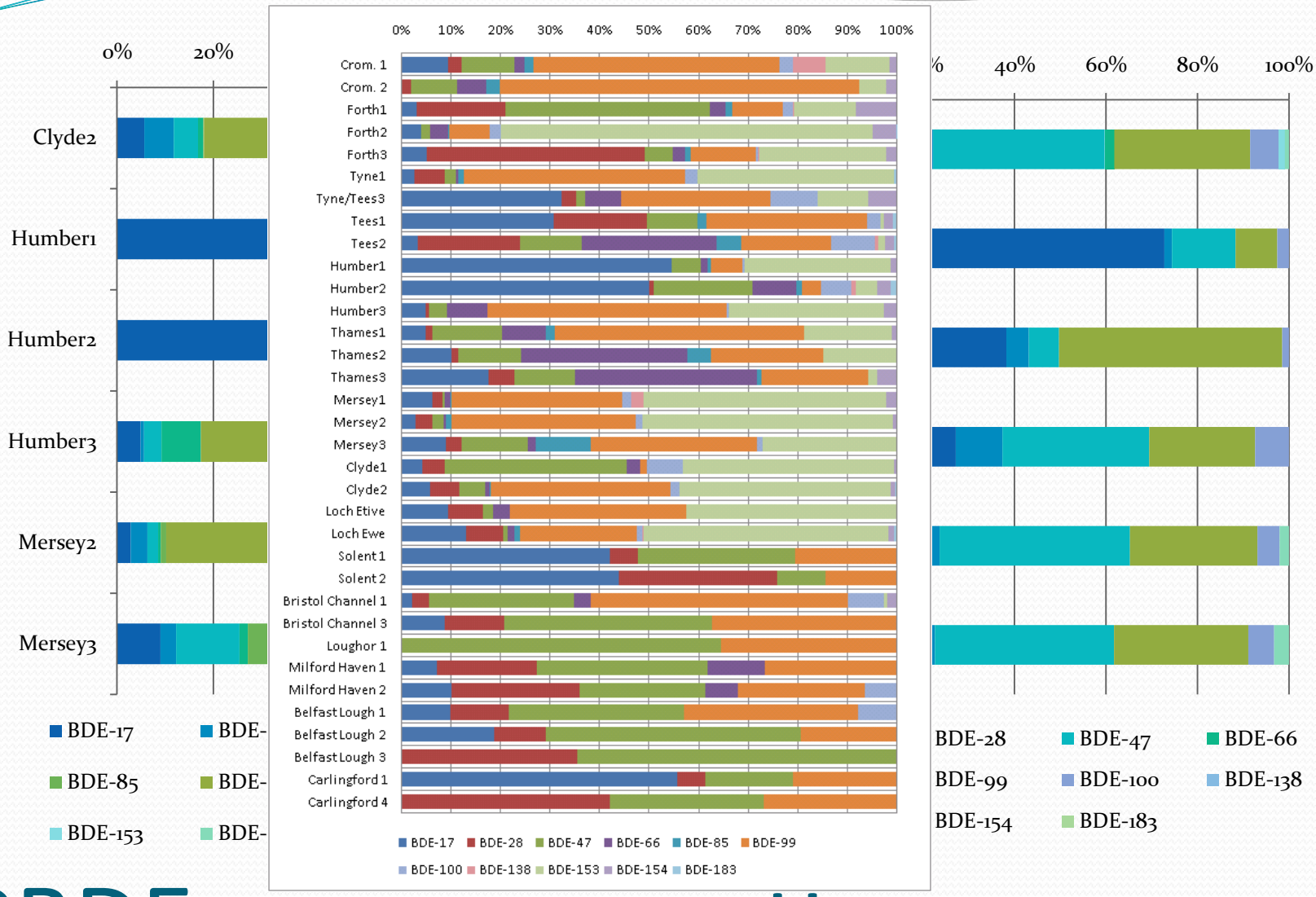
PCB in Mussels

Cefas

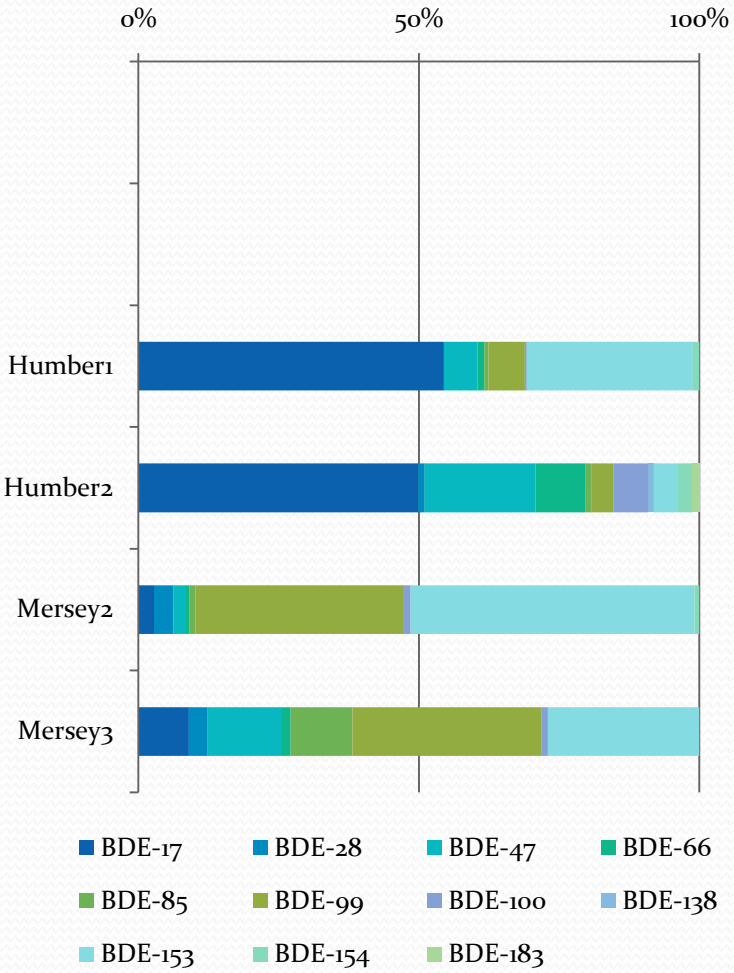


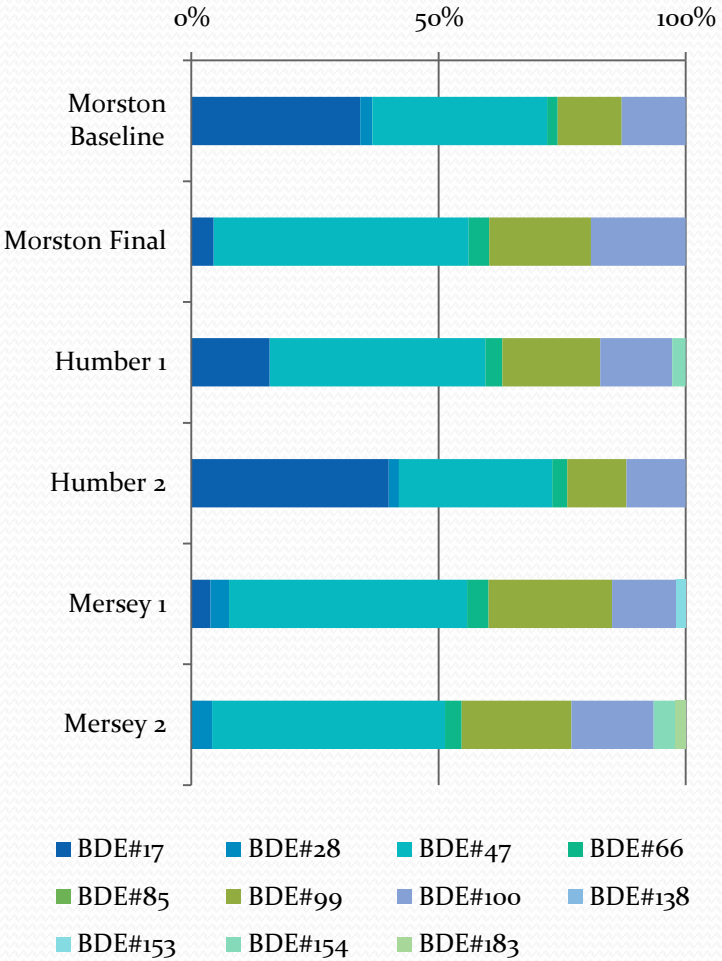
PBDE

Cefas

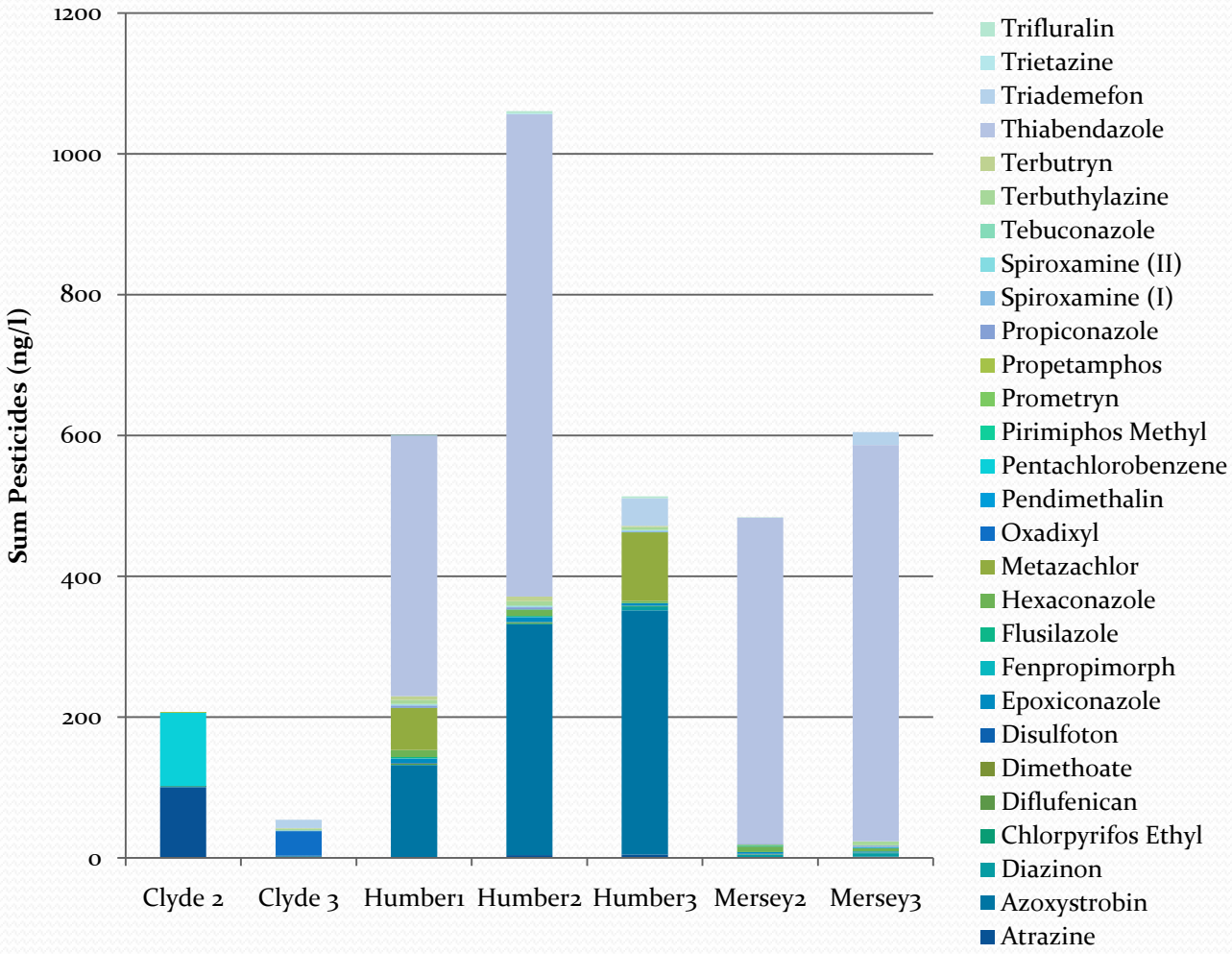


PBDE congener patterns



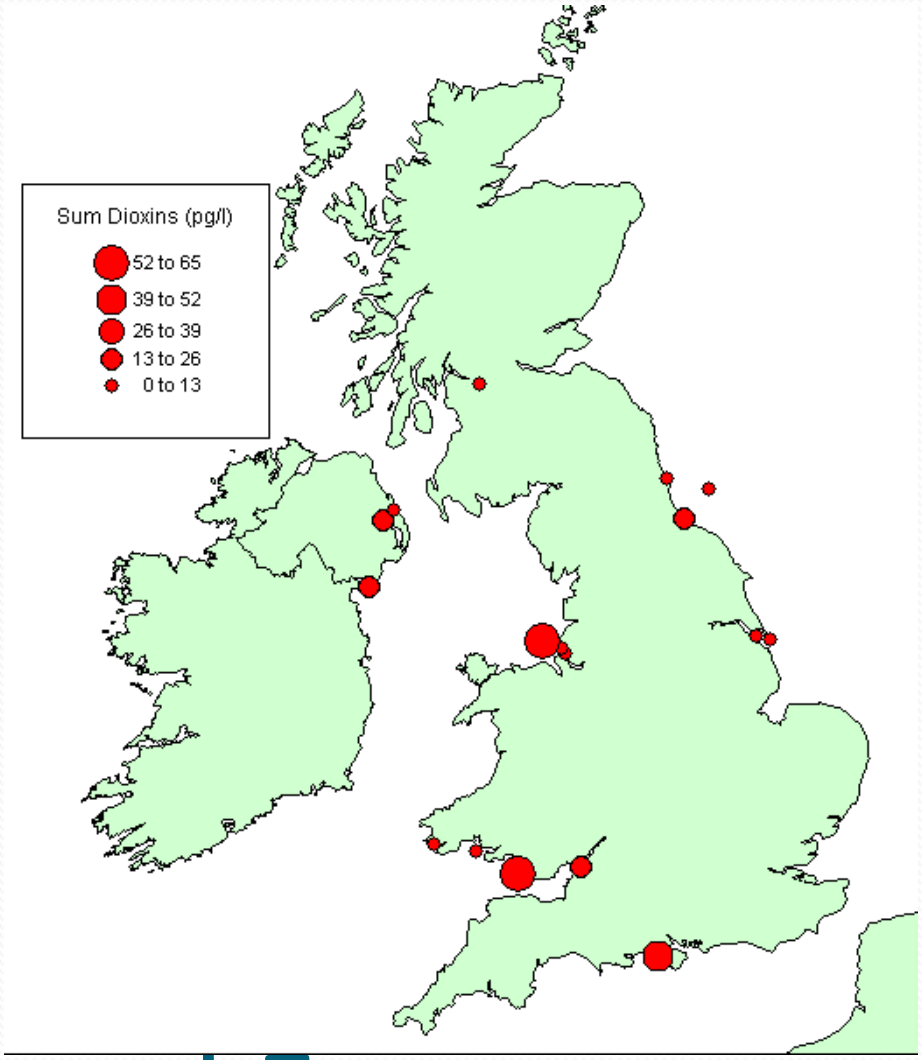


PBDE in samplers v mussels



Pesticides

Cefas



Dioxins and Furans

Cefas

- PAHs and PCBs relatively easy – done previously
- PBDEs high recovery/coelution of ISTD
- TBT – no recovery of ISTD or analytes
- Phthalates – everywhere
- APs – no reported problems
- Biocides – no reported problems but some v low Kow compounds, would not expect to see
- Dioxins – low recoveries of some stds

- Some Kpw not previously determined
- Not a specific method
- Sampling rates not well determined at some sites
- Oyster embryo studies showed no effects

Analytical Challenges

Cefas

- Carried out by Deltares
  - Phthalates
  - Musks
  - Chlorobenzenes
  - Chlorinated pesticides
  - Phosphates
  - PCBs
  - Pharmaceuticals/PCPs
- Method developed for specific extraction of TBT

Kpw determination and TBT

Other Challenges

- Few offshore sites available
- Permission to deploy in certain areas not easily obtained
- Some samplers lost
- Very long sampling programme
- POCIS gave useful data but not quantifiable
- Making sense of the results
  - Some compounds don't have partition coefficients
  - Results tend to be lower than we are used to seeing for 'total water'
  - Not able to compare with other monitoring data due to lack of similar sites

Cefas

Significance of results

- EQS values are based on ‘total’ water concentrations
- E.g. for nonylphenol 1 µg/l
- Includes dissolved, associated with SPM and DOC
- Highest value in this study ~5 ng/l (0.005 µg/l)
- Is this ‘safe’
- Data assessment
  - Step change in thinking required to analyse these results in terms of ‘allowable concentrations’
  - Needs to link to biota concentrations AND effects.

Cefas

- Many compounds measured using a single extraction (cf many extractions using water or biota).
- Lower detection limits achieved
- Measurable concentrations of most compounds found both onshore and offshore (due to high vol extracted).
- Smaller differences than usually observed between sites due to changing sampling rates (taking into account availability of compounds).
- Good comparability on 2 sampling occasions (limited study sites)
  - Site specific congener profiles
- Comparable with data from mussels

Progress made

Cefas

Sampling for WFD

Collaboration with UK Environment Agency

- Sites relatively easier to find/visit
- Biota not present/not consistent
- Need a surrogate for biota concentrations?
- EQS levels are set for water (AA and MAC)
- Based on total water concentrations (except metals)
- Compliance monitoring
- Trend monitoring
- Need good LODs

WFD specific challenges

Cefas

- 22 sampling sites throughout Thames (freshwater to marine)
- Collect:
  - Water
  - Sediment
  - Biota (caged)
  - Passive samplers
- Try to correlate concentrations

Approach

Cefas

- Can answer many questions
- Are they the same questions that are being asked?
- Can we change the questions?
- Are we able to use this technique for compliance/trends or as a surrogate?

Passive Sampling

Cefas