Analysis of organic contaminants in marine environment: development of automated systems for sampling and Stir Bar Sorptive Extraction

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A little about Cedre…

- CEDRE was created in 1978, as one of a follow-on measures after the Amoco Cadiz wreck (227 000 tons of crude oil spilled at sea in northern Brittany)
- Non for profit private structure funded by French government and industry
- Main officies in Brest
- 50 people staff
- Cedre is responsible, at national level, for documentation, research and experimentation on all polluting substances, on their effects on the environment and on specialized methods and equipment for mitigation of their environmental effects at sea and in inland waters

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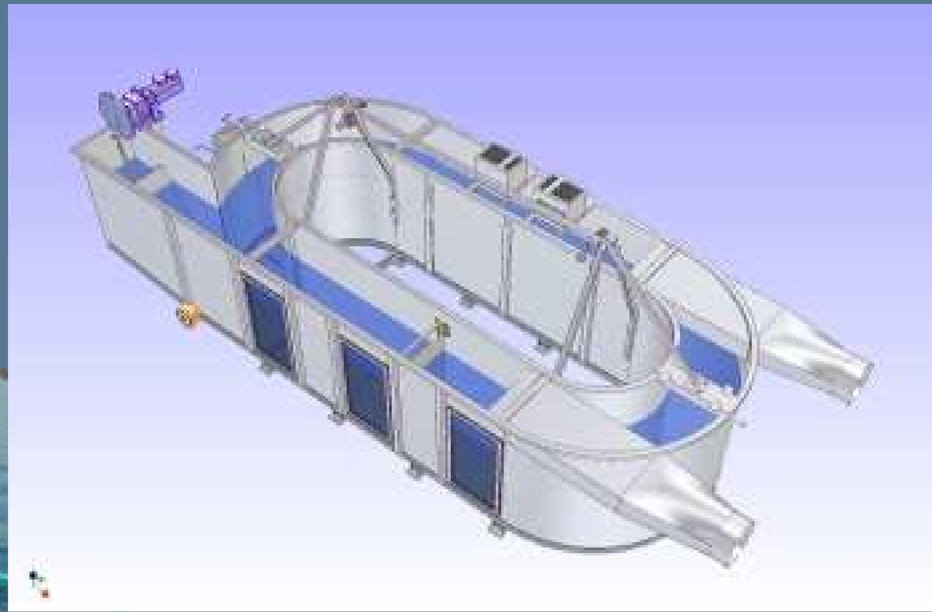
Main activities

- Domains
  - Research and development
  - Test and evaluation of equipment and products (potential pollutants and response products)
  - Post pollution monitoring, environmental impact assessment
  - Emergency response plans (private and public)
  - Training

- Interfaces
  - 24/7 service
  - Web site and paper publications (newsletter, operational guides, general information documents)

R&D activities



R&D activities

R&D activities…

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SBSE at *Cedre*

- In collaboration with *Ifremer* since the beginning (2003)
- Two main areas:
  - Application in the field of the technique in the framework of monitoring studies
  - Development of automated systems for water sampling and on site extraction

- *Cedre*'s needs:
  - Support for experimental studies (mainly ecotoxicity tests) conducted on PAHs, pendimethalin, …
  - Operational protocols for accidental water pollution

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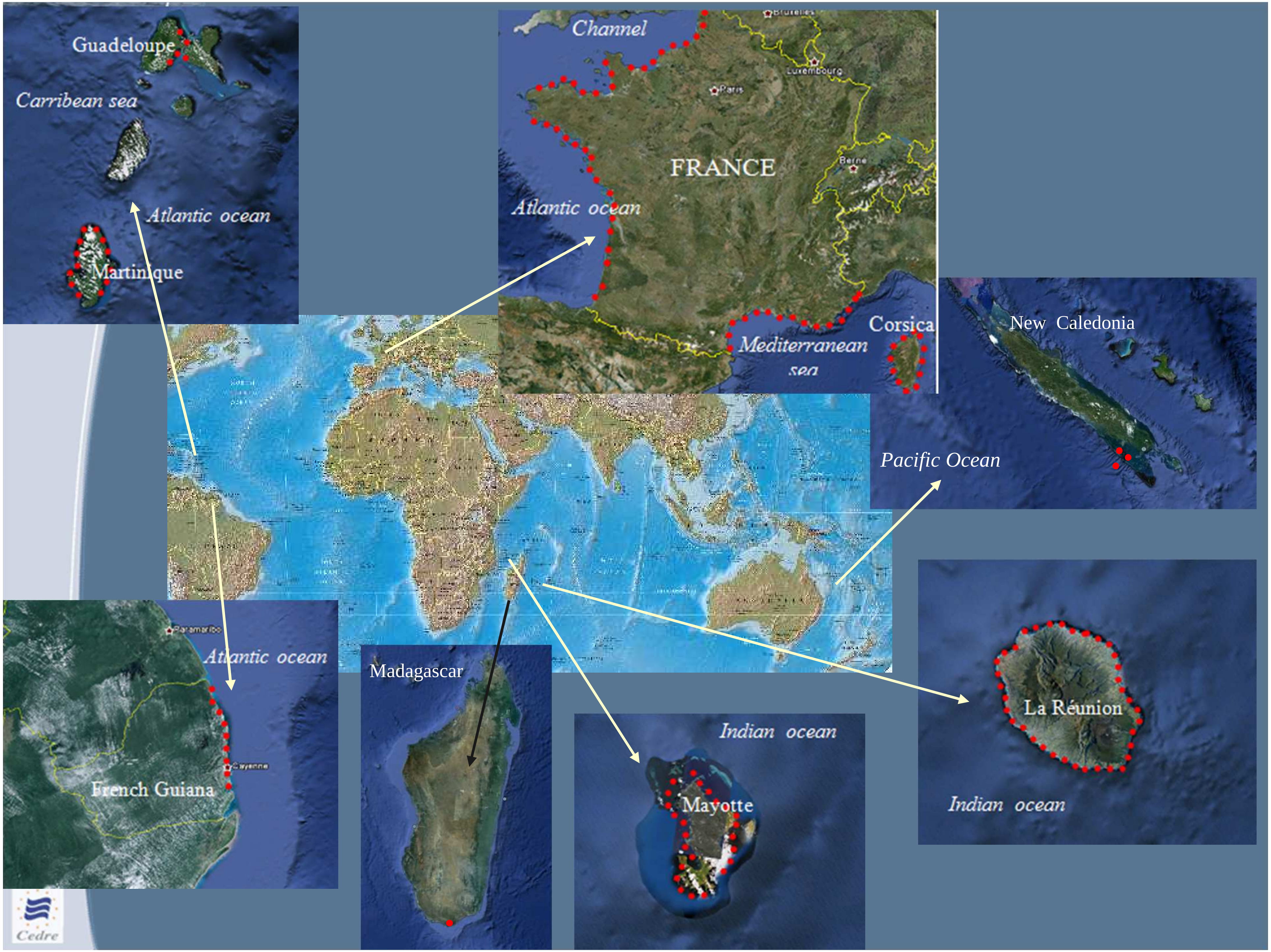
Monitoring studies

Combination of passive samplers:

- **POCIS** (Polar Organic Chemical Integrative sampler) EPOC-LPTC (Bordeaux I university)
- **DGT** (Diffusive Gradients in thin-film) Ifremer

and **SBSE** (Stir Bar Sorptive Extraction) Cedre


Guadeloupe
Carribean sea
Atlantic ocean
Martinique
Channel
Paris
Luxembourg
Berne
FRANCE
Atlantic ocean
Corsica
Mediterranean
sea
New Caledonia
Pacific Ocean
Paramaribo
Atlantic ocean
Cayenne
French Guiana
Madagascar
Indian ocean
Mayotte
La Réunion
Indian ocean
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Limits of quantification

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PAHs	LOD (ng/L)	LOQ (ng/L)
Naphthalene	0,16	0,54
Benzothiophene	0,07	0,22
Biphenyle	0,06	0,20
Acenaphtylene	0,06	0,21
Acenaphtene	0,06	0,20
Fluorene	0,06	0,19
Dibenzothiophene	0,08	0,27
Phenantrene	0,08	0,28
Anthracene	0,06	0,21
Fluoranthene	0,07	0,24
Pyrene	0,07	0,23
Benzo[a]anthracene	0,06	0,21
Chrysene	0,06	0,21
Benzo[b+k]fluoranthene	0,36	1,22
Benzo[e]pyrene	0,06	0,20
Benzo[a]pyrene	0,06	0,19
Perylene	0,06	0,19
Indeno(1,2,3-cd)pyrene	0,17	0,57
Benzo(g,h,i)perylene	0,16	0,52

PCBs	LOD	LOQ
PCB 7	0,13	0,44
PCB 28	0,06	0,21
PCB 35	0,06	0,21
PCB 52	0,06	0,20
PCB 101	0,09	0,31
PCB 105	0,13	0,44
PCB 118	0,14	0,48
PCB 135	0,14	0,48
PCB 138	0,20	0,66
PCB 153	0,21	0,72
PCB 156	0,27	0,91
PCB 180	0,35	1,17

Pesticides	LOD	LOQ
Alpha-BHC	0,07	0,24
β+γ-BHC	0,07	0,22
Delta-BHC	0,15	0,51
Aldrine	0,07	0,24
Isodrine	0,07	0,22
Endosulan	0,11	0,37
Dieldrine	0,11	0,37
Endrine	0,23	0,77
4,4'-DDT	0,20	0,67

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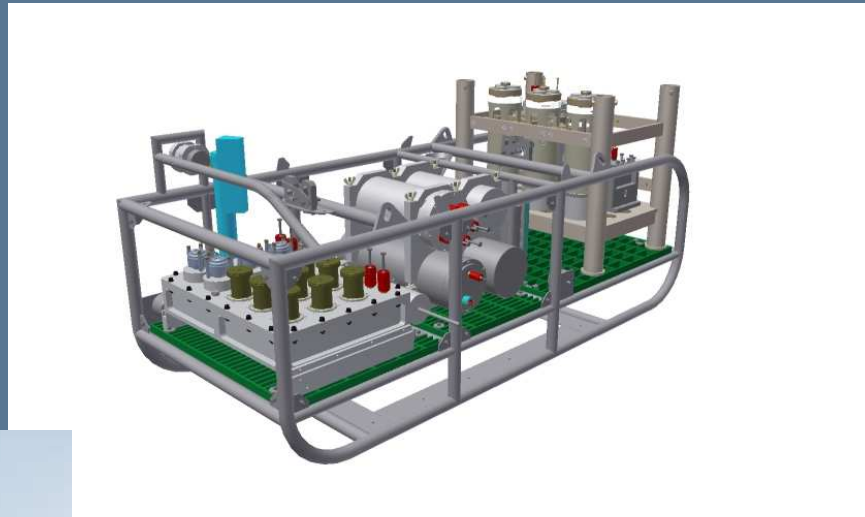
Automation of the SBSE

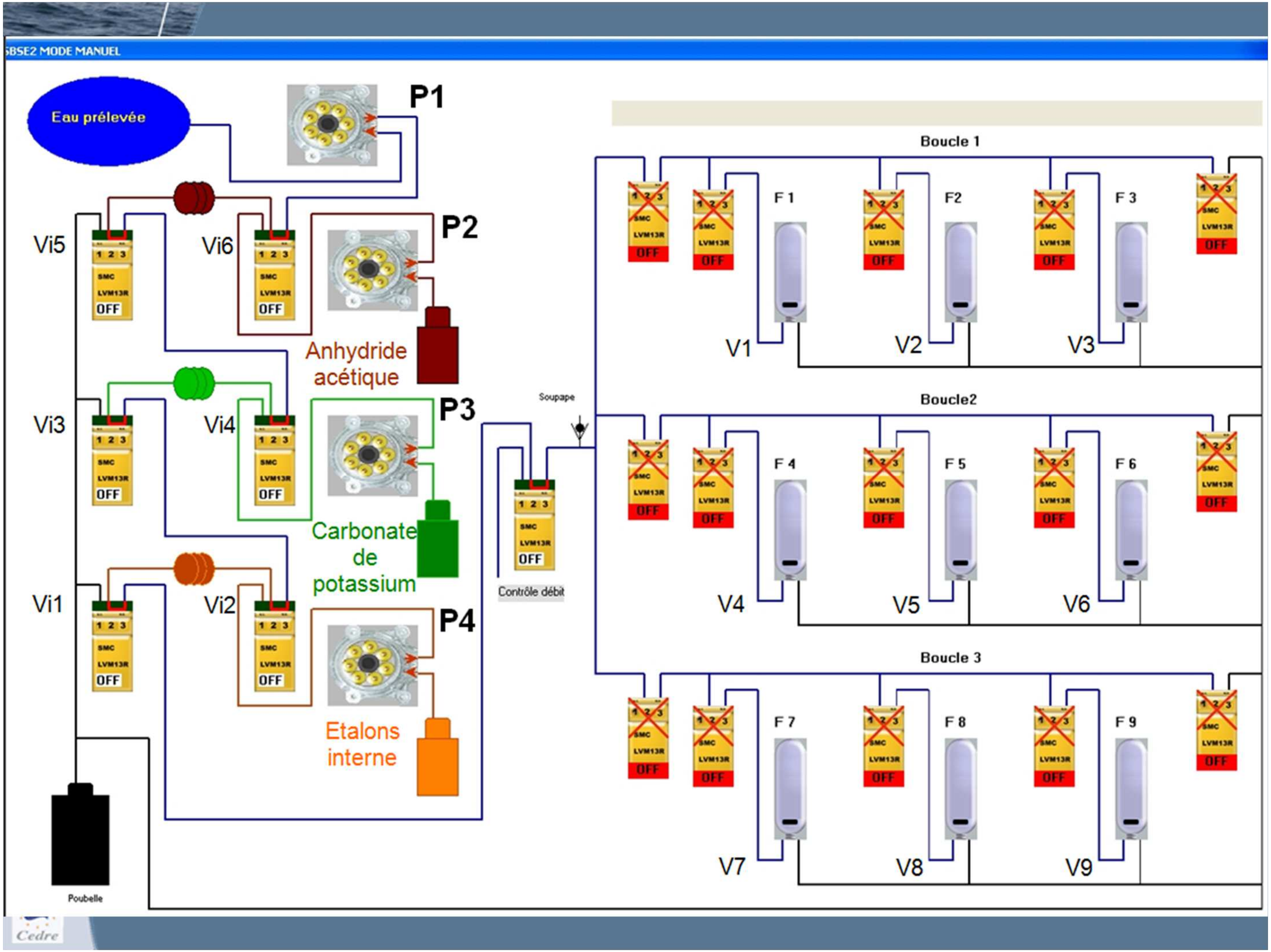


INSTITUT CARNOT
Ifremer EDROME

Automation of the SBSE

Automation of the SBSE

Automation of the SBSE


SBSE2 MODE MANUEL
Eau prélevée
P1
P2
P3
P4
Vi5
Vi6
Vi3
Vi4
Vi1
Vi2
Anhydride acétique
Carbonate de potassium
Etalons interne
Poubelle
Soupape
Contrôle débit
Boucle 1
Boucle2
Boucle 3
F 1
F2
F 3
F 4
F 5
F 6
F 7
F 8
F 9
V1
V2
V3
V4
V5
V6
V7
V8
V9
SMC
LVM13R
OFF
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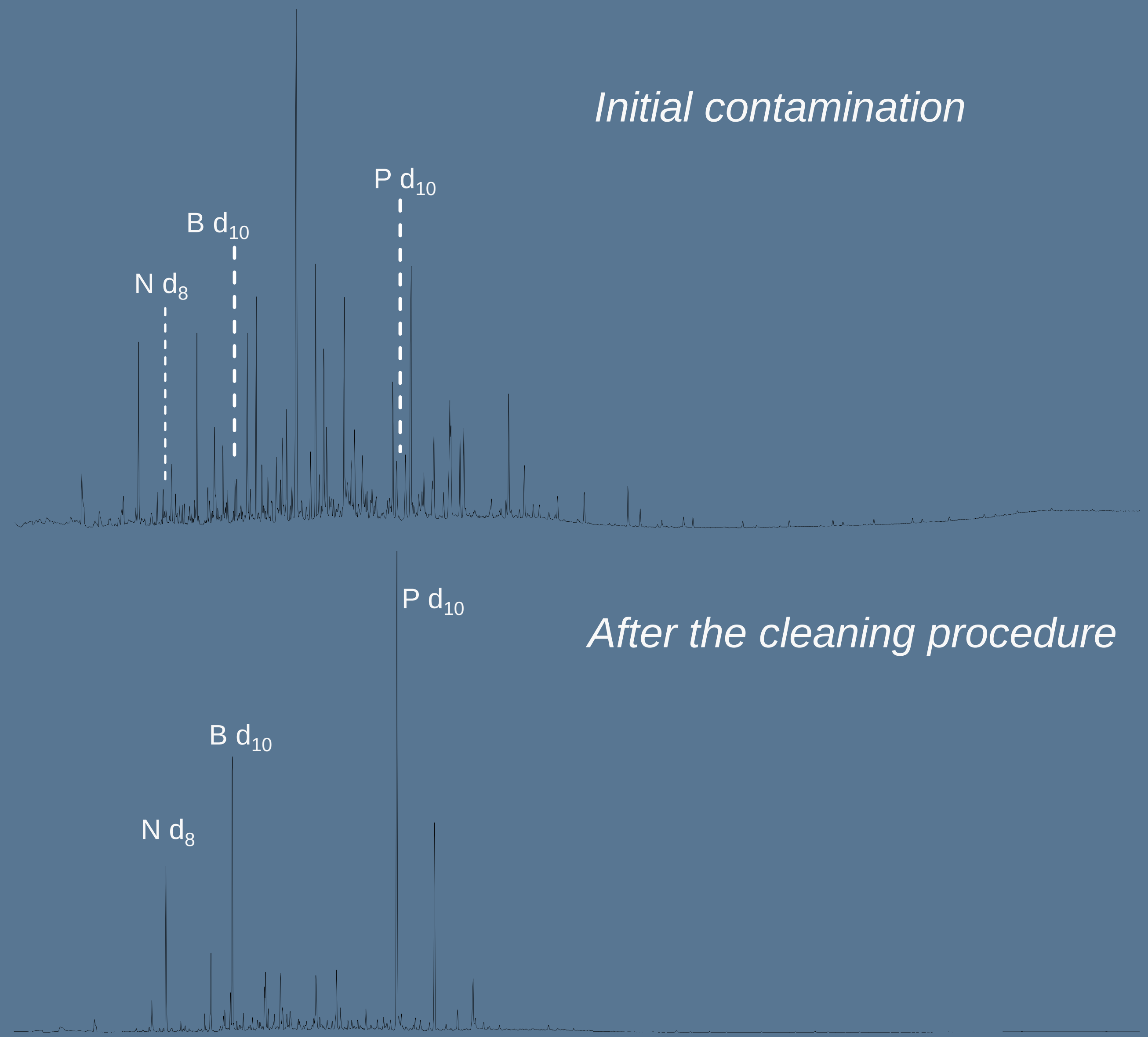
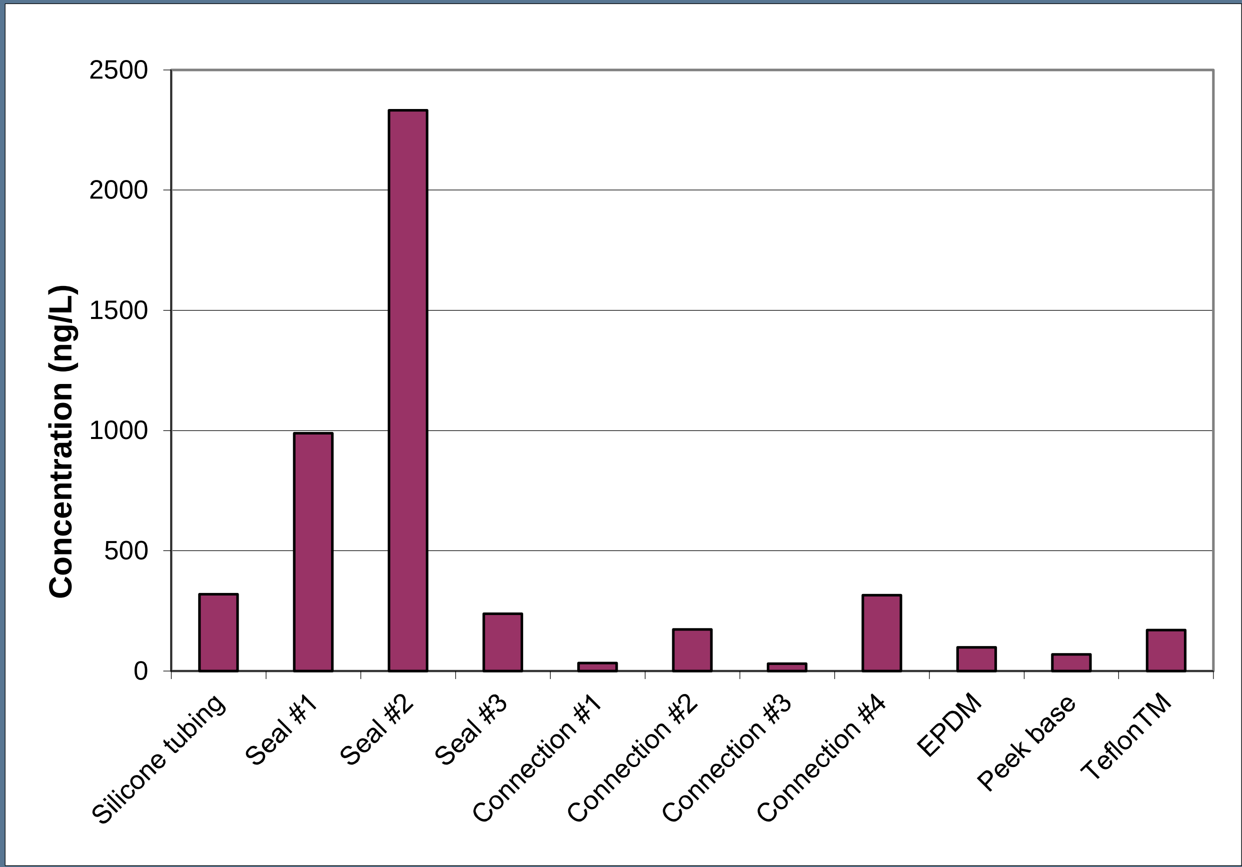
Automation of the SBSE



Automation of the SBSE

Validation of materials during the design phase (example of Bisphenol A)



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Application to monitoring studies

Limits of quantification

Compounds	$LQ_{laboratory}$ (ng/L)	LQ_{device} (ng/L)	EQS (ng/L)
PAHs	0.04 - 0.3	0.2 - 1.1	2 - 2400
Pesticides	0.03 - 0.4	0.1 - 1.1	5 - 600
PCBs	0.02 - 0.1	0.2 - 1.0	1
Chlorophenols	0.1 - 0.6	0.3 - 1.2	200 - 1000

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Development of simple procedures for SBSE in *non classic* conditions

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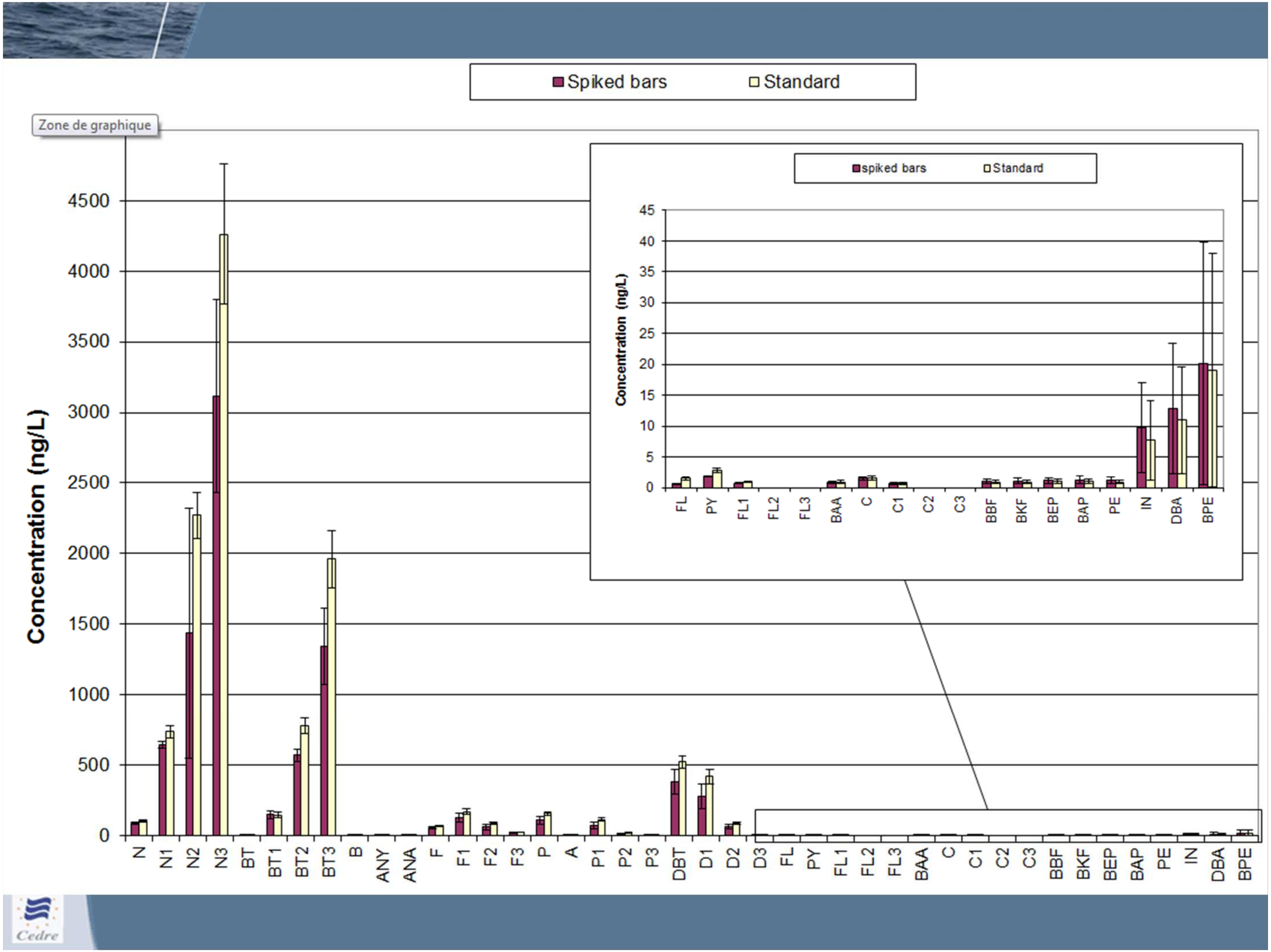
Gülser Ana (Madagascar, 2009):

Need for PAHs analyses at low levels (potential contamination of drinking water)

Difficulty of sending chemicals onsite (MeOH and Internal Standard)

Possibility of spiking bars with IS prior to shipment?


Spiked bars
Standard
Zone de graphique
Concentration (ng/L)
4500
4000
3500
3000
2500
2000
1500
1000
500
0
N N1 N2 N3 BT BT1 BT2 BT3 B ANY ANA F F1 F2 F3 P A P1 P2 P3 DBT D1 D2 D3 FL PY FL1 FL2 FL3 BAA C C1 C2 C3 BBF BKF BEP BAP PE IN DBA BPE
spiked bars
Standard
Concentration (ng/L)
45
40
35
30
25
20
15
10
5
0
FL PY FL1 FL2 FL3 BAA C C1 C2 C3 BBF BKF BEP BAP PE IN DBA BPE
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SBSE applied to hydrocarbons

Compounds	Abbreviation	US EPA list	Sulphur compounds	Other parent PAHs	Alkyl derivatives
Naphthalene	N	✓			
C_1-Naphtalene	N1				✓
C_2-Naphtalene	N2				✓
C_3-Naphtalene	N3				✓
Benzo(b)thiophene	BT		✓		
C_1-Benzothiophene	BT1				✓
C_2-Benzothiophene	BT2				✓
C_3-Benzothiophene	BT3				✓
Biphenyl	B			✓	
Acenaphtylene	ANY	✓			
Acenaphtene	ANA	✓			
Fluorene	F	✓			
C_1-Fluorene	F1				✓
C_2-Fluorene	F2				✓
C_3-Fluorene	F3				✓
Dibenzothiophene	D		✓		
C_1-Dibenzothiophene	D1				✓
C_2-Dibenzothiophene	D2				✓
C_3-Dibenzothiophene	D3				✓
Phenanthrene	P	✓			
Anthracene	A	✓			
C_1-Phenanthrene/Anthracene	P1				✓
C_2-Phenanthrene/Anthracene	P2				✓
C_3-Phenanthrene/Anthracene	P3				✓
Fluoranthene	FL	✓			
Pyrene	PY	✓			
C_1-Fluoranthene/Pyrene	FL1				✓
C_2-Fluoranthene/Pyrene	FL2				✓
C_3-Fluoranthene/Pyrene	FL3				✓
Chrysene	C	✓			
C_1-Chrysene	C1				✓
C_2-Chrysene	C2				✓
C_3-Chrysene	C3				✓
Benzo[a]anthracene	BA	✓			
Benzo[b+k]fluoranthene	BBF+BKF	✓			
Benzo[e]pyrene	BEP			✓	
Benzo[a]pyrene	BAP	✓			
Perylene	PE			✓	
Indeno(1,2,3-cd)pyrene	IN	✓			
Dibenz(a,h)anthracene	DBA	✓			
Benzo(g,h,i)perylene	BPE	✓			

41 molecules or groups of molecules

LOQ ≈ 1 ng/L for each compound

Internal standards: perdeuterated PAHs

Analysis of bioaccumulated PAHs

(Alkaline digestion and SBSE-TD-GC/MS/MS)

1 g (fresh tissue)

10 mL EtOH + 500 mg KOH
+ Internal Standards

80℃ / 3 hours

+ 100 mL water

SBSE extraction

2 hours

TD-GC/MS/MS analysis

Analysis of bioaccumulated PAHs

(Alkaline digestion and SBSE-TD-GC/MS/MS)

<u>Parent PAHs</u>:

- Calibration curves obtained with individual compounds
- Quantifier / Qualifier to avoid matrix effects
- LOQ ≈ 1 ng/g (<u>in theory</u>)

<u>PAHs and OH-PAHs in biological samples</u>:

- Fast, simple and avoid great volumes of solvent
- Need for *in situ* derivatization
- Alternative method for smaller samples (100 mg)

Conclusion & Perpectives

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Traces levels methods in water:

- Very simple & sensitive technique
- From GC/MS to GC/MS/MS
- Phtalates, PBDE, pharmaceutical products…

Automation of the SBSE:

- Field validation
- Multi-step extraction for an integrative approach
- Used as passive sampler?

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