Biomonitoring strategy of chemical pollution along the Iberian Mediterranean Coast: Development of the MED POL approach

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Environmental assessment component
Mediterranean Action Plan
MED POL PROGRAMME
BARCELONA CONVENTION, 1976

MEDPOL Phase II (1981-1995):

TRACE METALS	Mercury Lead Cadmium Zinc Copper Arsenic Nickel Aluminium
ORGANOCHLORINATED COMPOUNDS	Polychlorinated byphenyls: CB28, CB52, CB101, CB105, CB118, CB138, CB153, CB156, B180.
	pp 'DDE, *pp* 'DDT y *op* 'DDT
	γ -Hexachlorocyclohexane
	α -Hexachlorocyclohexane
	Hexachlorobencene
	Transnonachlor
	Dieldrin
	Aldrin
POLYCYCLIC AROMATIC HYDROCARBONS (PAHs)	Phenanthrene
	Anthracene
	Fluoranthene
	Pyrene
	Benzo[a]anthracene
	Chrysene
	Benzo[e]pyrene
	Benzo[b]fluoranthene
	Benzo[k]fluoranthene
	Benzo[a]pyrene
	Benzo[g,h,i]perylene
	Dibenzo[a,h]anthracene
	Indeno[1,2,3-c,d]pyrene

Network initiated in 1991 by IEO (OC of Murcia)

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Biomonitoring strategy for chemical pollution

MEDPOL Phase III (1996-2005):

Mussels Network
Mytilus galloprovincialis

Research field studies using
Mullus barbatus

Selected contaminants

+

Biomarkers
(UNEP/RAMOGE, 1999)

Marine Ecosystem approach: MPIs	
Biological indicators	
Number of exotic species (all taxa)	
Number of zoobenthic species (S)	
Presence/abundance of sensitive/opportunixtic zoobenthic especies/taxa	
Community diversity (zoobenthos/phytobenthos)	
Presence and coverage of benthic macrophytes (sensitive/opportunistic):POMI	
Biotic index (EEI, BENTIX)	
Biomarkers	
Stress on stress (survival in air) in molluscs	
Lysosomal membrane stabililty in molluscs and fish cells	
Lipofucsin lysosomal accumulation in molluscs and fish cells	
Neutral lipid lysosomal accumulation in molluscs and fish cells	
Frequency of micronuclei in molluscs and fish cells	
DNA damge in molluscs and fish cells	
Peroxisome proliferation	
Methallothionein in molluscs cells	
AChE in molluscs	
EROD activity	
Chemical indicators	
Referred to hardazous substances	HMB = heavy metals in Biota
	HME= Heavy metals in Effluent
	HMS = Heavy metals in sediment
	OCB = Organichlorines in Biota
	OCE = Organochlorines in Effluent
	OCS = Organochlorines in Sediment
	PHS = Petroleum Hydrocarbons in Sediment
	PHB = Petroleum hydrocarbons in Biota
	PHE = Petroleum hydrocarbons in Effluent
	BBW = Bacteria in bathing waters
	BSW = Bacteria in shellfish growing waters
Referred to eutrophication	Chl = Chlorophyll a
	NO3, NO2, NH4 = Nitrates, Nitrites and Ammonium
	PO4 = Orthophosphates
	N, P = Total N and Total P
	Tr = Transparency
	BOD = Biological Oxygen Demand
Referred to the marine environment related to Climate Change	T/S = Temperature and Salinity
	DO = Dissolved oxygen
	Si = Orthosilicic acid

MEDPOL Phase IV (2006-2013):

Strategy for the development of Mediterranean Marine Pollution Indicators **(MPIs),** (UNEP, 2003)

Extended monitoring: Since 2006

Biomonitoring programme conducted by MCBE (IEO) along the Mediterranean coast: Main goals

Spatial distribution → Mussels (Cont/Biom)
Spatial distribution → Red mullet(Cont/Biom)

Temporal trend → Mussels (Cont/Biom)
Temporal trend → Red mullet(Cont/Biom)
Temporal trend → Sediments(Cont)

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- Determination of **spatial distribution** and **temporal trends** of **chemical contamination** in coastal and references areas by using **target organisms** (red mullet and mussels) and **sediments**.

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- Determination of **spatial distribution** and **temporal trends** of **chemical contamination** in coastal and references areas by using **target organisms** (red mullet and mussels) and **sediments**.

- To seek evidences of detrimental **biological effects** in **target especies** and monitor them over time.

Sampling fields

Sampling strategy: UNEP/FAO/IOC/IAEA, 1984; UNEP, 2006 and ICES, 2005

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FREQUENCY AND SAMPLING SEASON

Temporal trend monitoring in biota: Yearly

Temporal trend monitoring in sediment: Once at least 5 years

Spatial monitoring: Once every 5 years

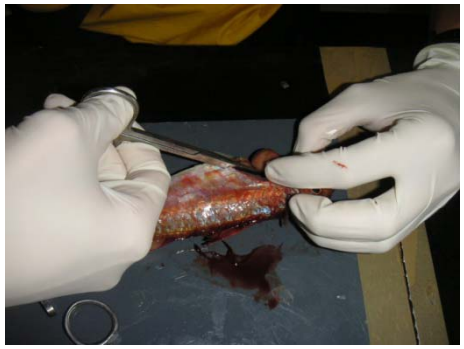
- The samples of *Mullus barbatus* and sediments are collected in **April** (non-matured specimens).

- The samples of *Mytilus galloprovincialis* are collected from **mid May to mid June** (no-spawning period).

CHEMICAL CONTAMINANTS

Recommendations of MEDPOL Programme and also considering OSPAR.

Use of reference materials, **QUASIMEME** and **IAEA** intercomparison exercises



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AAS: Graphite furnace, flameless atomic.

Cold vapour technique

GC: ECD-MS detector, helium carrier gas

HPLC: UV detector, water-methanol gradient phase

BIOMARKERS

Analysed following recommendations of MEDPOL Programme.

BEQUALM and **MEDPOL** (Prof. A. Viarengo)

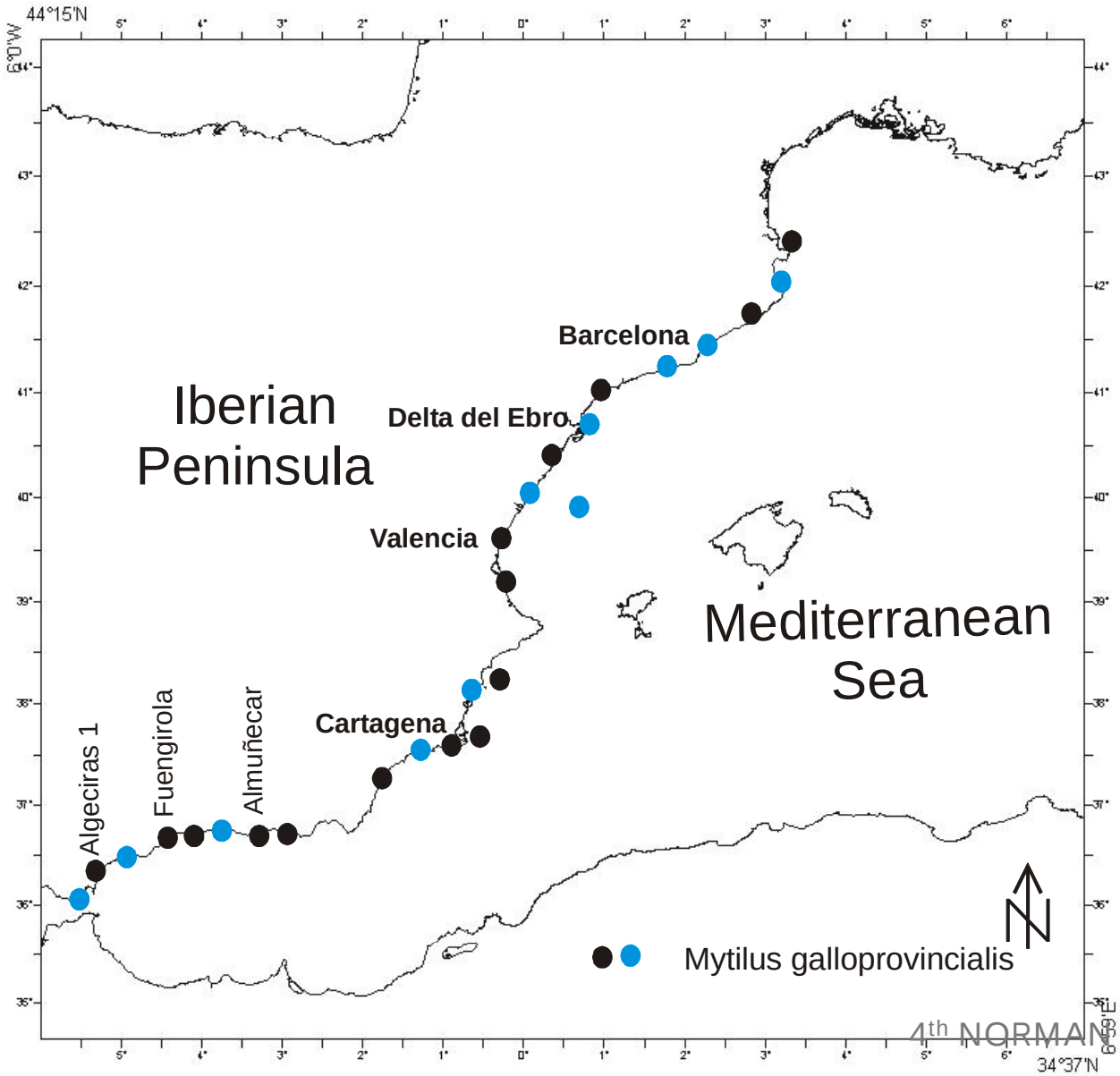
Mussel

- Stress on Stress
- Stability lysosomal
- Micronuclei
- AChE
- Metallothioneins

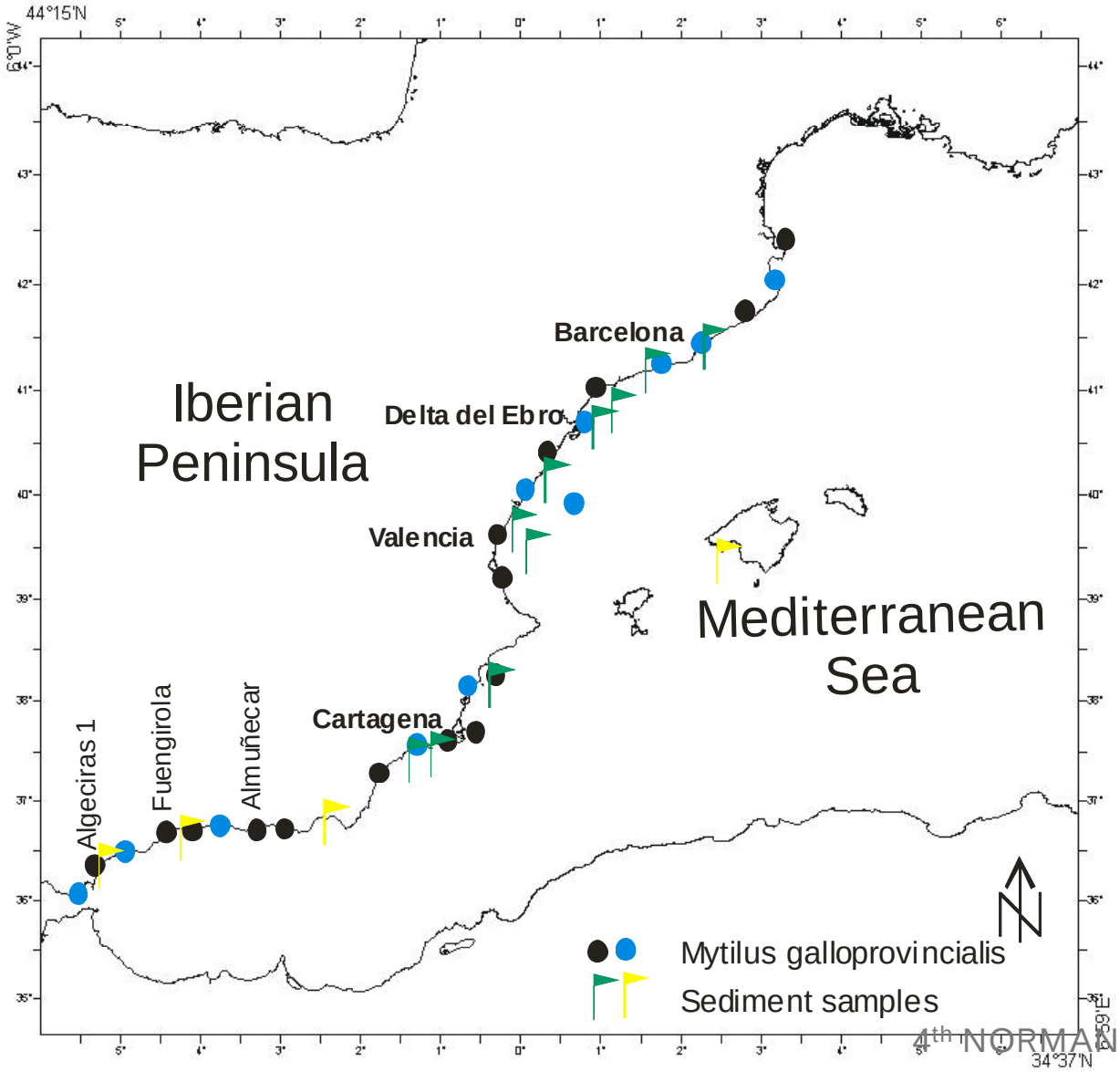
Red mullet

- Genotoxic damages
- EROD
- Micronuclei
- AChE
- Metallothioneins

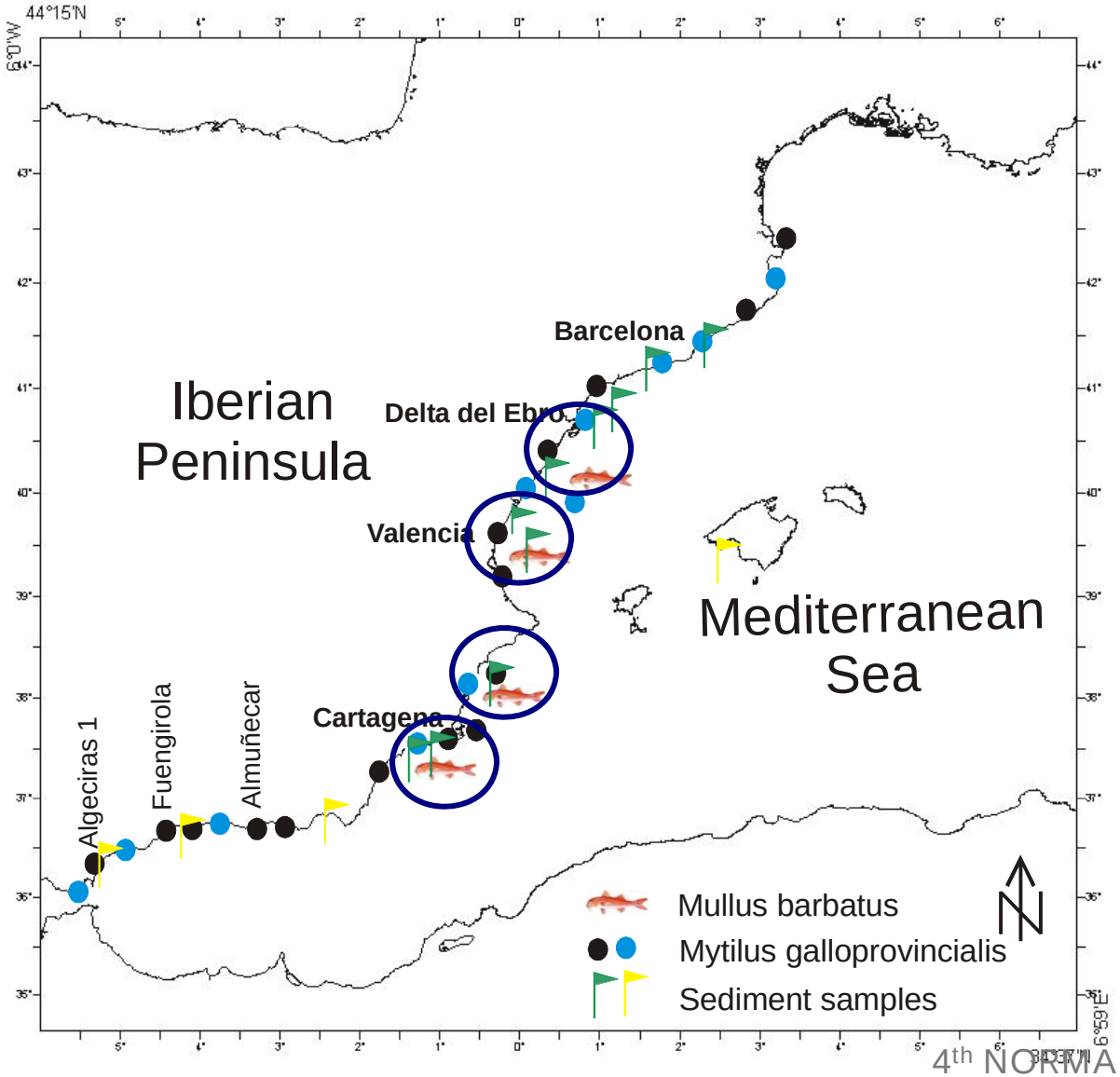
Mussel sampling fields



Sediments sampling fields (2006-2010)



Fish sampling areas 2006



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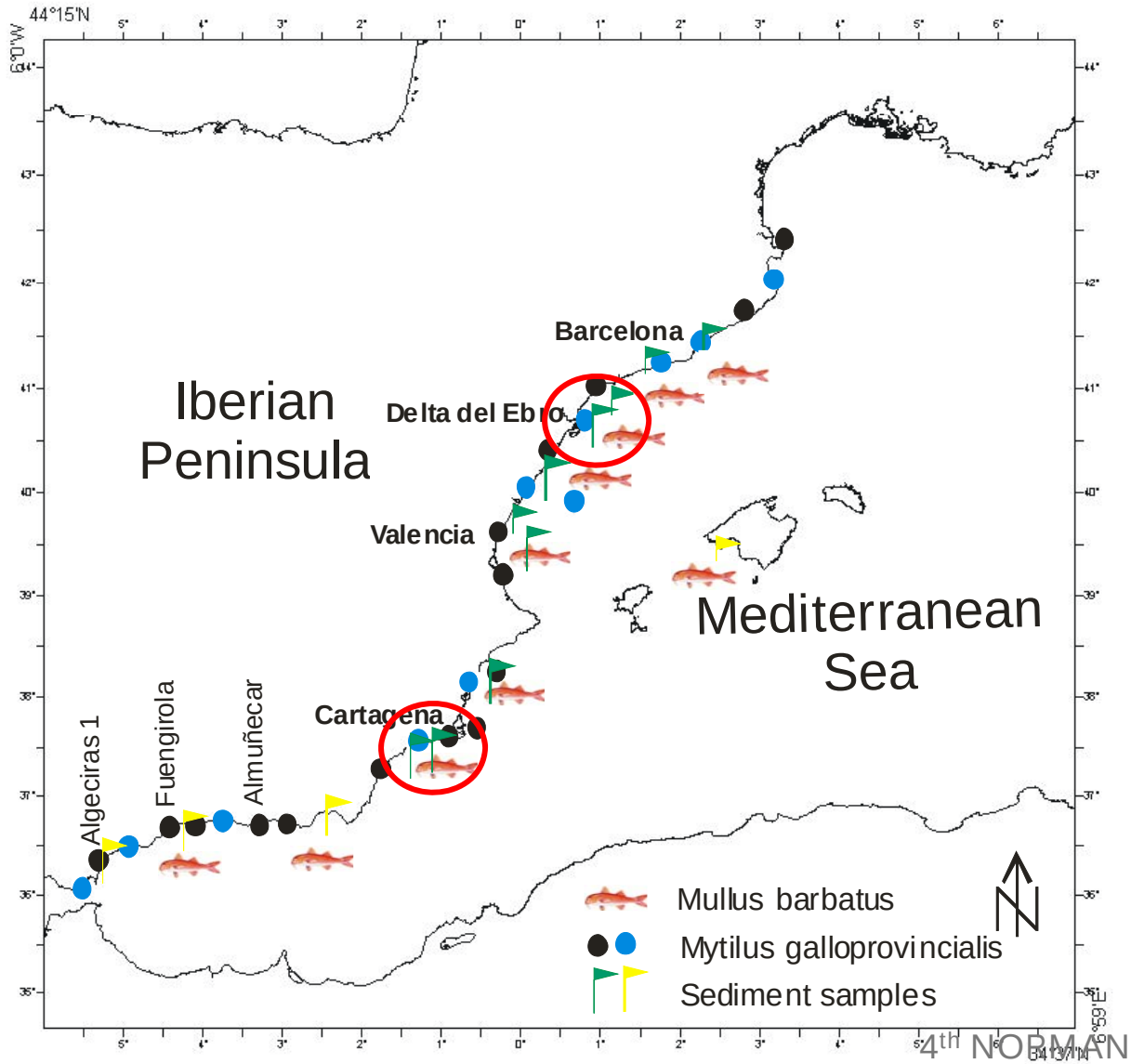
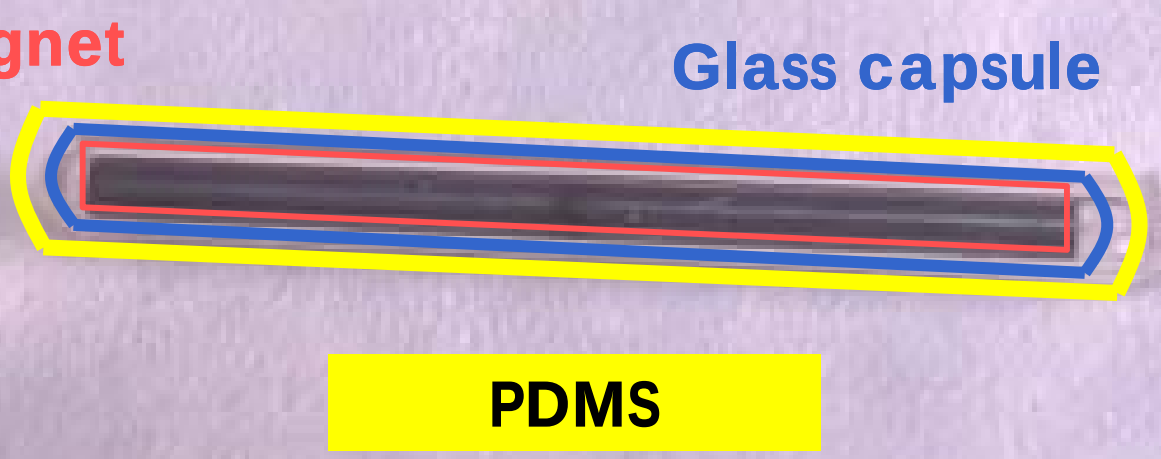


EMERGING CONTAMINANTS
UNEP, 2007

Stir Bar Sorptive Extraction, SBSE

- Low volume
- No dissolvents
- Volatile and semi volatile compounds
- Automatic way
- Lower manipulation



Stir Bar Sorptive Extraction, SBSE

(Pérez-Carrera *et al.*, 2007).

100 mL sample **+**

Stir Bar (2 cm)

SEA WATER

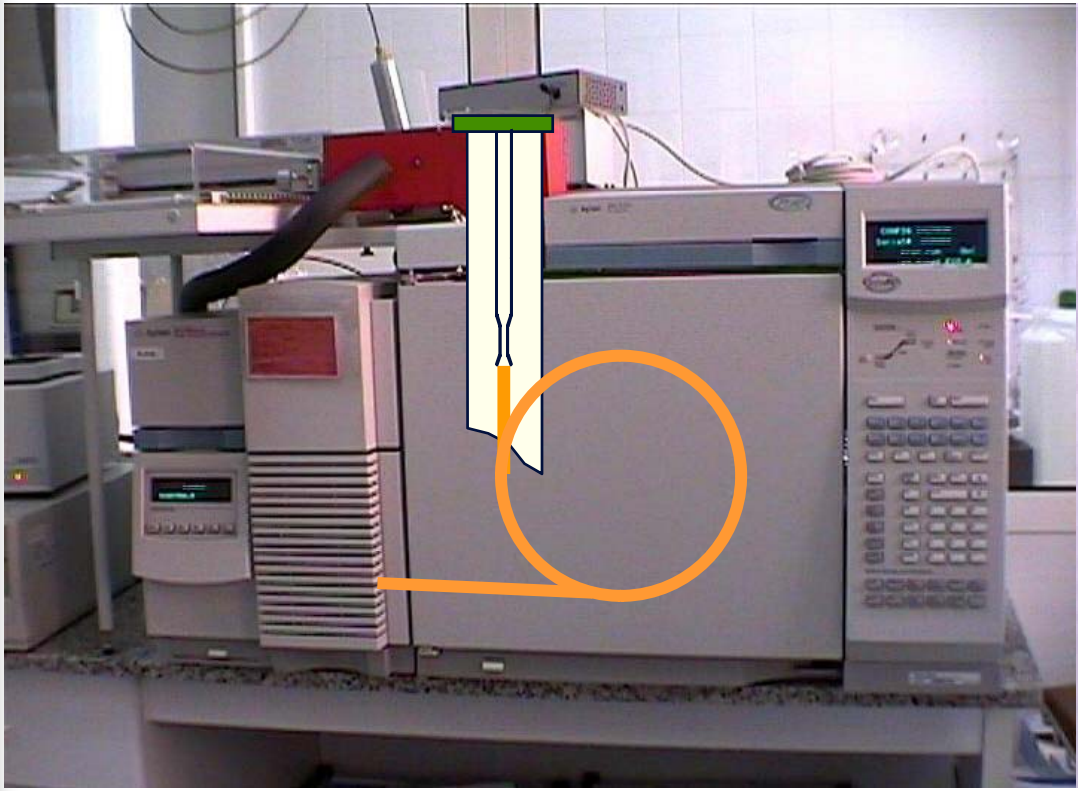
10 mL sample **+**

Stir Bar (1 cm)

INTERSTITIAL WATER

Potential application to solid samples analysis (sediment and biota) using low volume extracts

SBSE/GC/MS

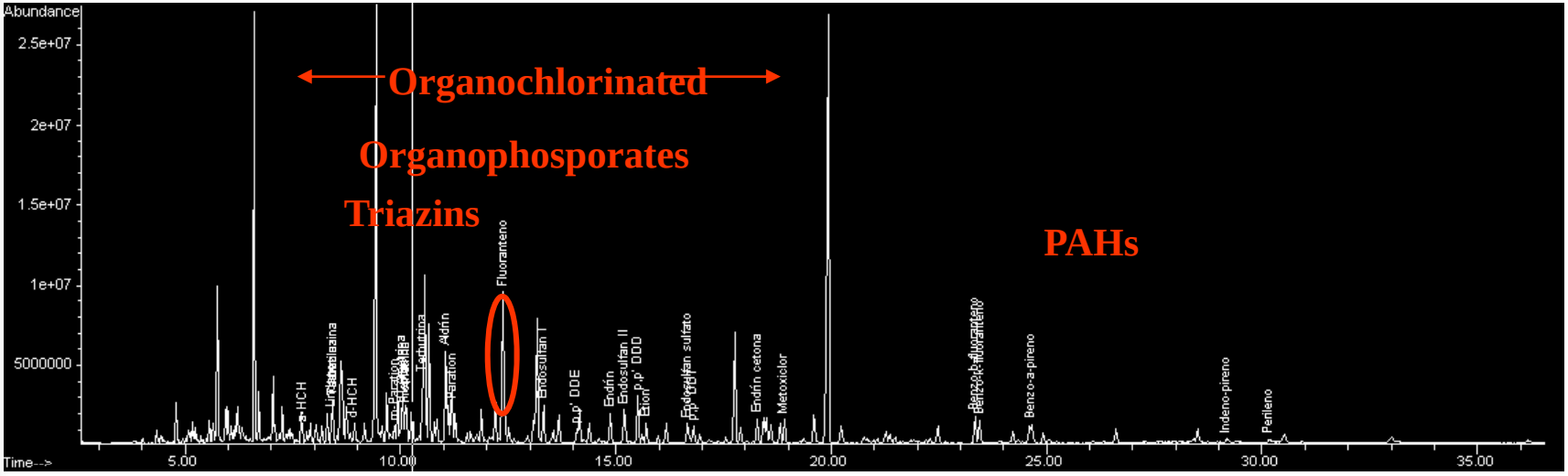


Programmable injector of Vaporization Temperature (PTV)

Advantages: **Higher polymer volume than SPME: Better sensitivity**

SBSE/GC/MS

Simultaneous analysis of PAHs, PCBs, organochlorinated pesticides, organophosphorates, triazines in sea water and/or intersticial water (Pérez-Carrera *et al*., 2007).



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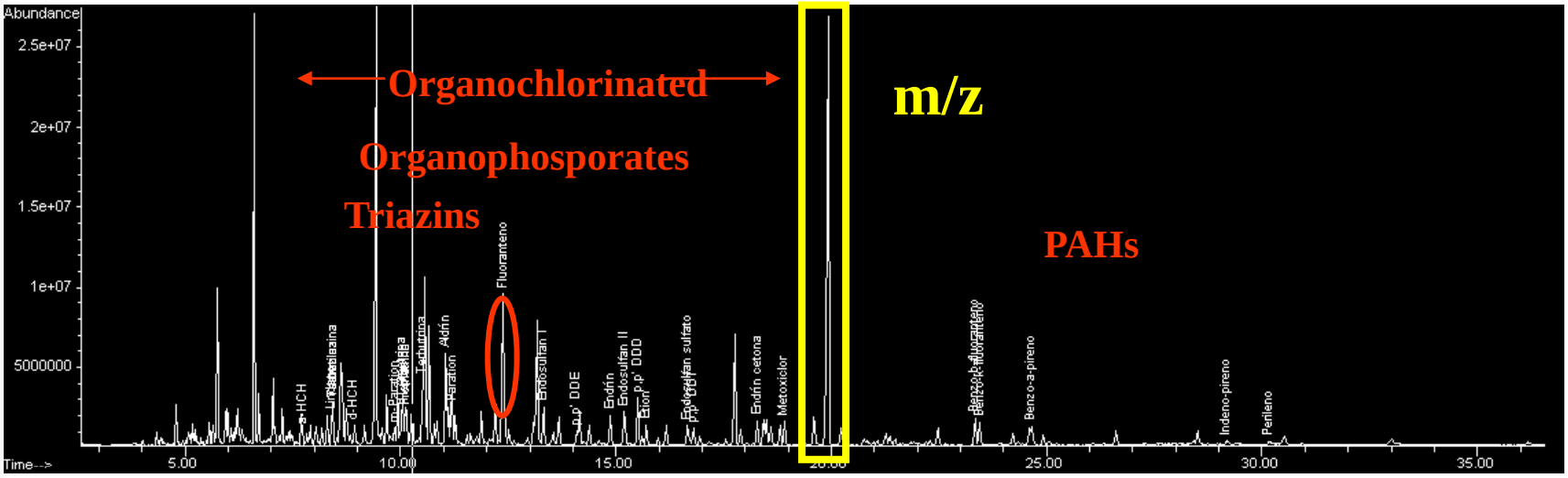
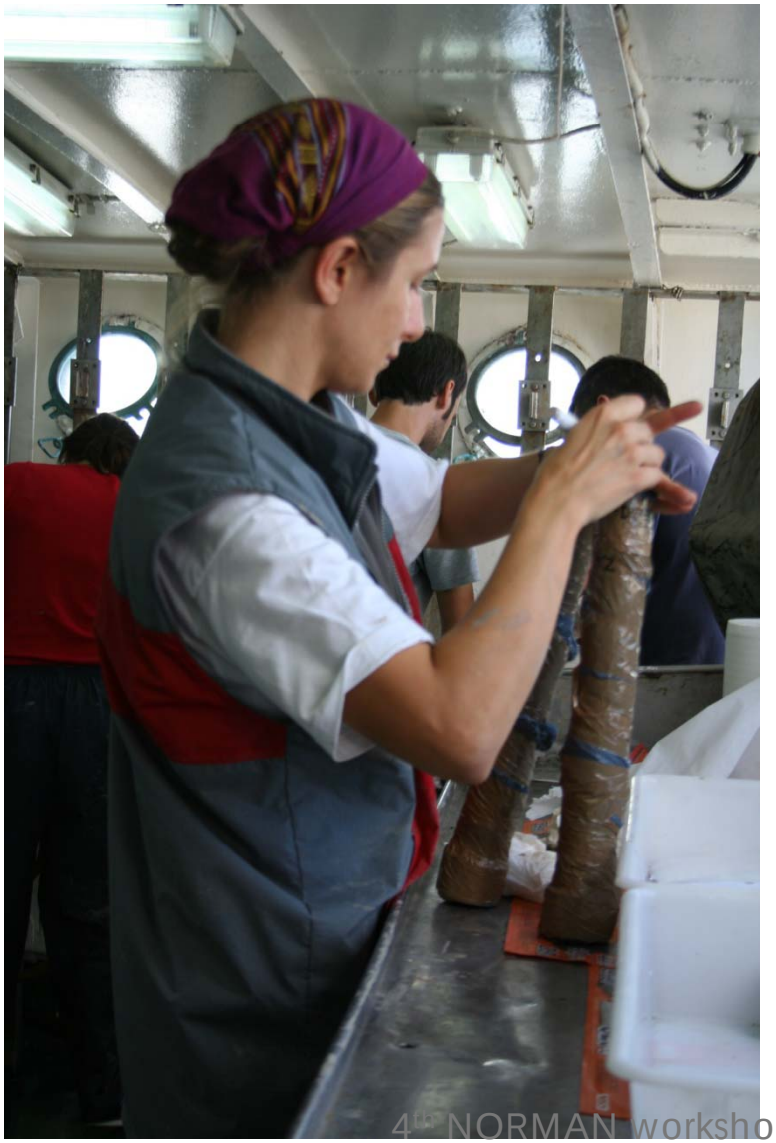
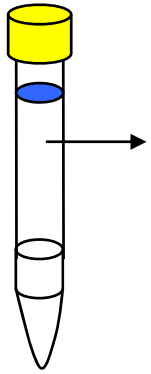


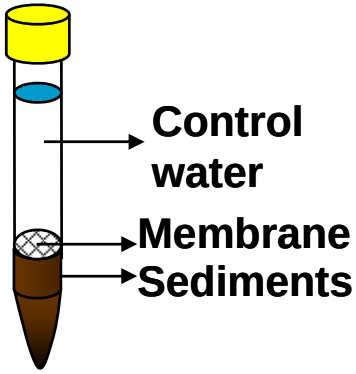
Emergent contaminant identification (restricted use pesticides, pharmaceutical products, organometallic compounds, etc).

Just starting …



Ecotoxicological assessment





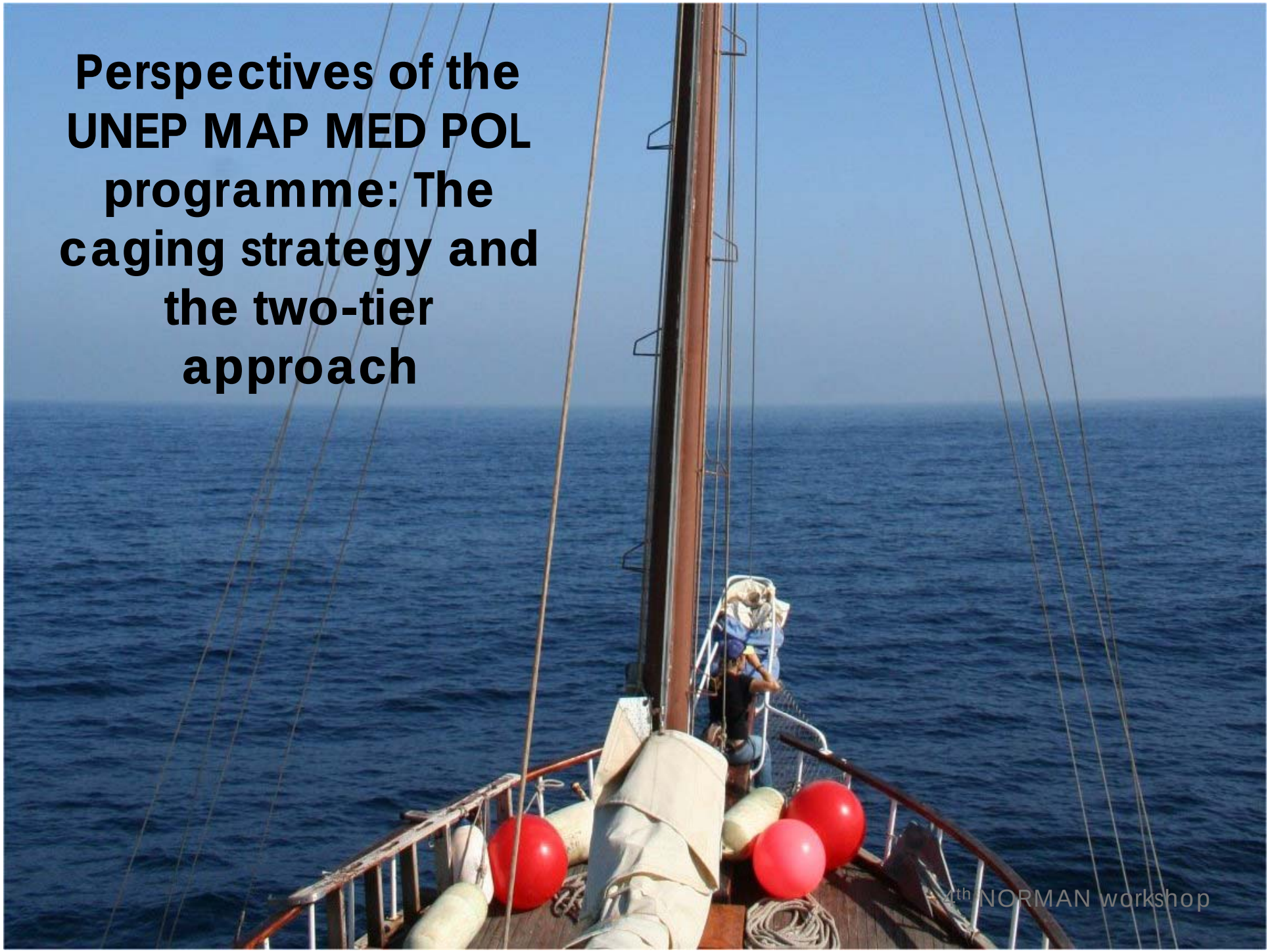
(Cesar et al., 2004; US EPA, 2002)

Future development using fish and sediments

- To progress sampling fish and sediments in different areas to identify those of concern for temporal trend monitoring and integrated assessment

- To progress with the ecotoxicological assessment of the sediment quality applying more bioassays

- To progress with the study of emerging contaminants in water and marine solid samples using the SEBS coupled to GC/MS


Perspectives of the UNEP MAP MED POL programme: The caging strategy and the two-tier approach
4th NORMAN workshop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Use of caged mussels: Considerations….

Use of models to validate and to normalise contaminant concentrations (Andral *et al*., 2004)

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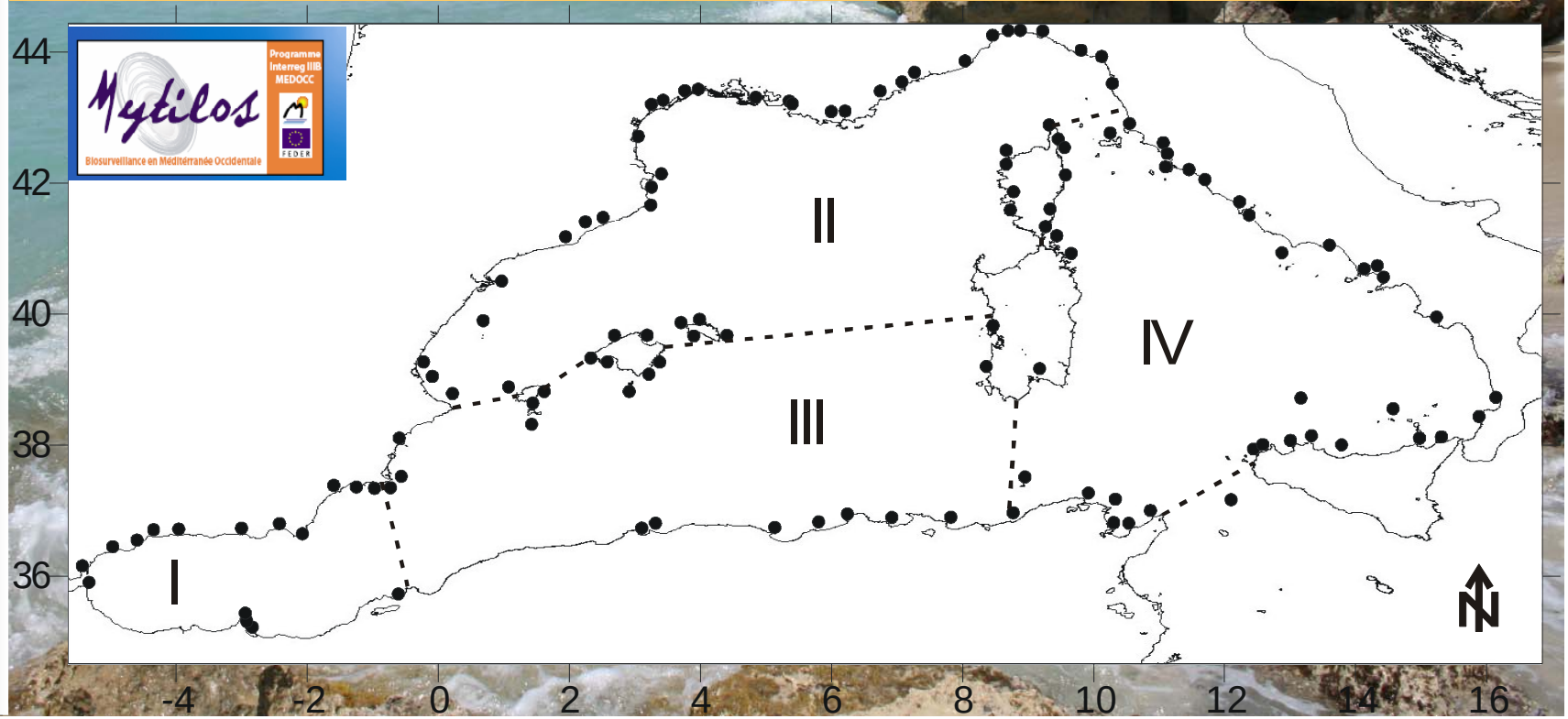
(MYTILOS project, INTERREG III B MEDOCC; http://mytilos.tvt.fr)



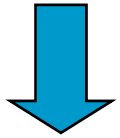
Two-tier approach: Level of pollutant-induced stress syndrome in target species (Viarengo et al., 2007. *Biochem. And Phisiol*)

1º Tier

SCREENING:

A) With the use of Lysosomal Membrane Stability (LMS) (Stress on stress) it is possible to identify pollutant-induced stress syndrome;

B) Data from mussel mortality indicate areas with high pollution



Simple- Cheap analysis

With 2 end-points = early warning + mortality

As a result of the TIER I analyses:

A) No effects on lysosomal membrane stability → clean sites → no other analysis necessary (biological or chemical);

B) Increased mortality → direct chemical analysis to identify that induce biological effects.

2º TIER

In sites where there are alterations in lysosomal membrane stability:

By utilising a battery of biomarkers (BEEP project- EU VI programme) it is possible to quantify the stress syndrome

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Proposal to include during MED POL phase IV the two-tier approach in national monitoring programmes using caged mussels (Alexandria, 2006).

Use of caged mussels: Considerations….

Exposure period of 3-4 weeks (Viarengo *et al*, 2007) to assess the level of pollutan-induced stress syndrome in mussels

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- Longer exposure period lasting several months to cover bioaccumulation and subtle chronic effects: to identify changes over time

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Longer exposure period lasting several months to cover bioaccumulation and subtle chronic effects: to identify changes over time

- **Higher cost strategy** for wide area biomonitoring programmes: Two field sampling and recovery is not guaranteed

Future development using mussels

- To continue using native mussels

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- To implement the use of caged mussels to solve the problem of scarcity

Immersion period: 1 year / 3 months / 30 days

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  to solve the problem of scarcity

  to assess the offshore water quality: MYTILOS approach

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- To implement the use of caged mussels

  to solve the problem of scarcity

  to assess the offshore water quality: MYTILOS strategy

  To validate the two-tier approach

Immersion period: 1 year / 3 months / **30 days**

PILOT STUDY USING CAGED MUSSELS

PILOT STUDY USING CAGED MUSSELS

To conduct an initial integrated chemical-biological effect assessment

- **Comparison between the MEDPOL integrated approach with that conducted by OSPAR**
- **Participating in harmonization exercises**

Ecosystem health approach:
Need for an integrated assessment

Higher harmonization of criteria among different regional programmes would be desirable

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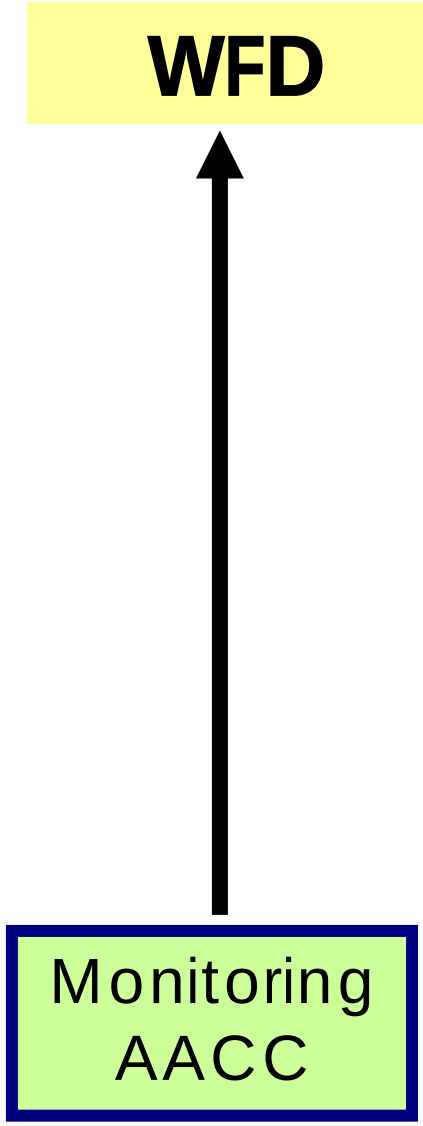
Higher harmonization of criteria among different regional programmes would be desirable

- Standardised samplings surveys in a coordinated way

ECOLOGICAL AND CHEMICAL STATUS



(Biological effects methods not prescribed)

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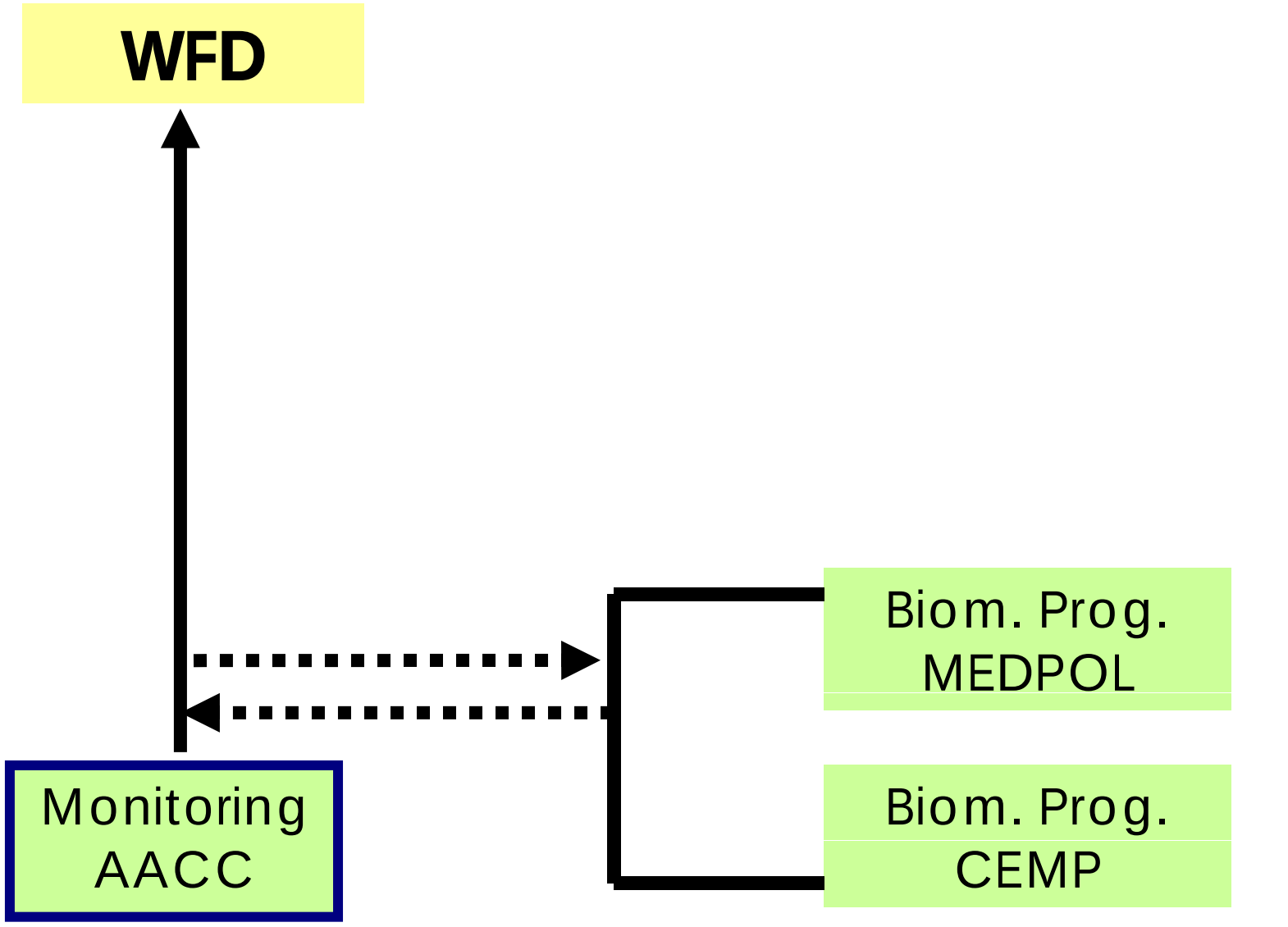

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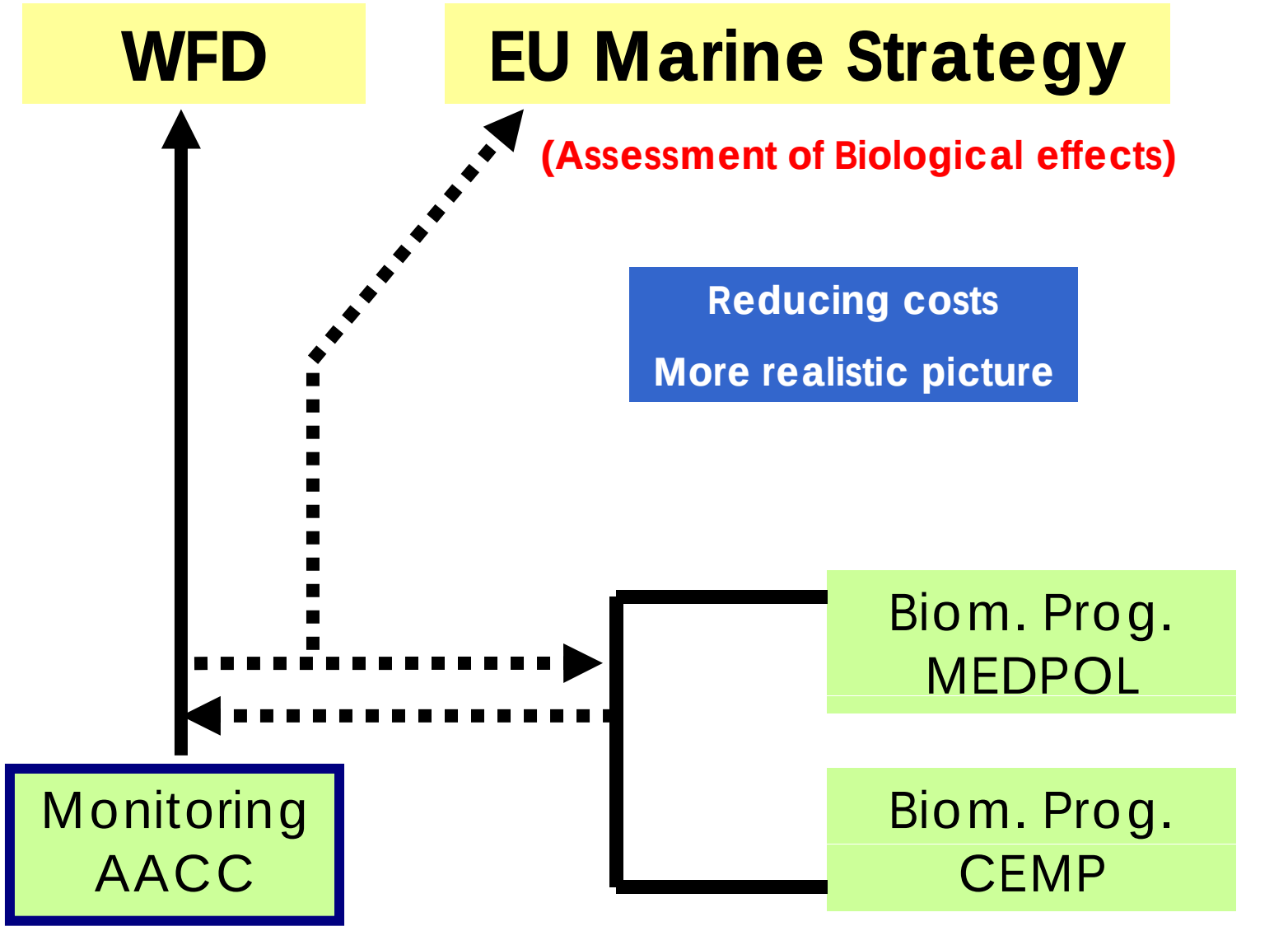


Ecosystem approach:
Need for an integrated assessment

Higher harmonization of criteria among different regional programmes would be desirable

- Standardised samplings surveys in a coordinated way

- Measurements can be shared and comparables

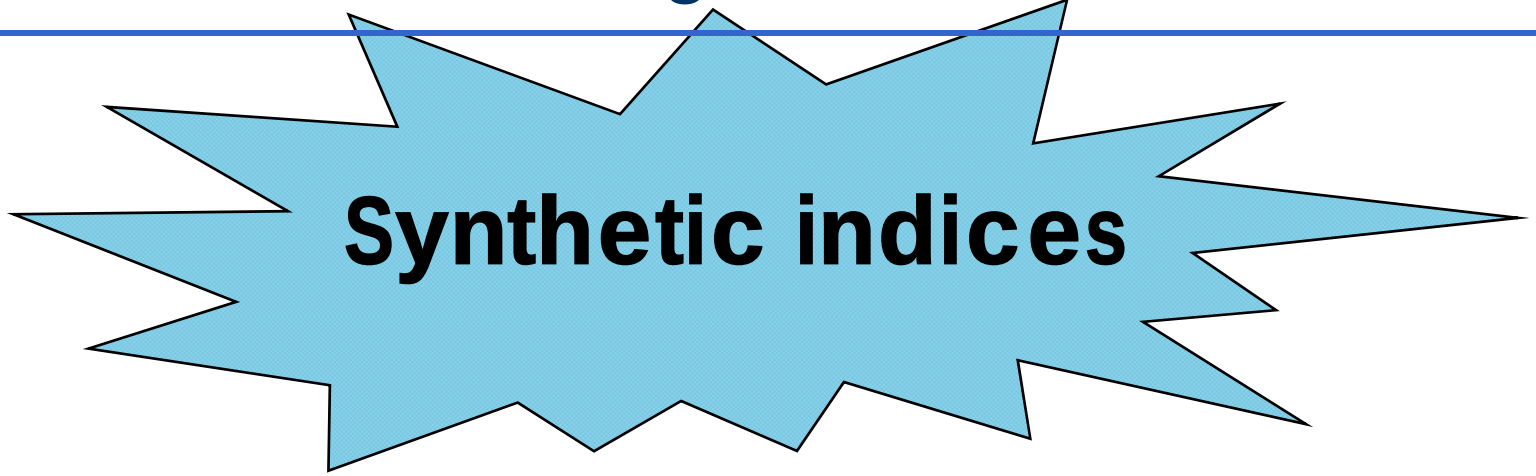
Ecosystem approach:
Need for an integrated assessment

Higher harmonization of criteria among different regional programmes would be desirable

- Integrate data to give an objective global evaluation of the prevalence situation regarding marine chemical contamination.

establishment of assessment criteria

Ecosystem approach:
Need for an integrated assessment

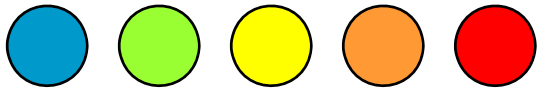


Ecosystem approach:
Need for an integrated assessment

Synthetic indices

Expert system(Dagnino et al., 2007)

Stress syndrome level (mussel biomarkers)



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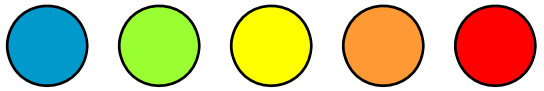
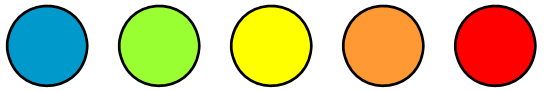


AMBI index (soft-bottom benthic communities)



Ecosystem approach:
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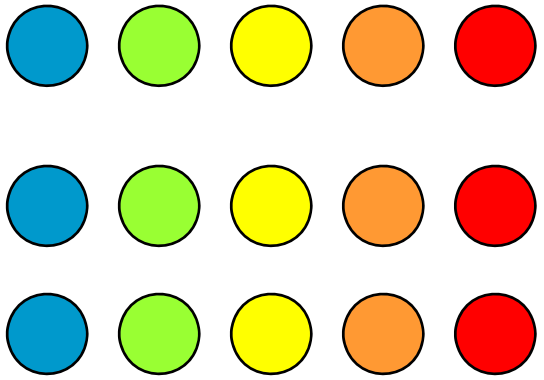
AMBI index (soft-bottom benthic communities)

POMI index (*Posidonia oceanica*)



Ecosystem approach:
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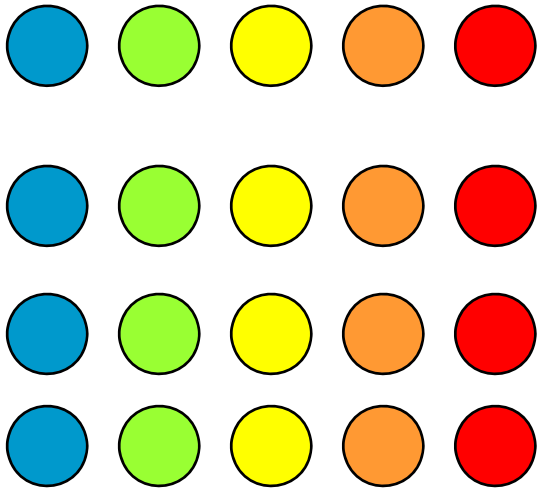
Synthetic indices

Stress syndrome level (mussel biomarkers)

AMBI index (soft-bottom benthic communities)

POMI index (Posidonia oceanica)

Coming indices...



Ecosystem approach:
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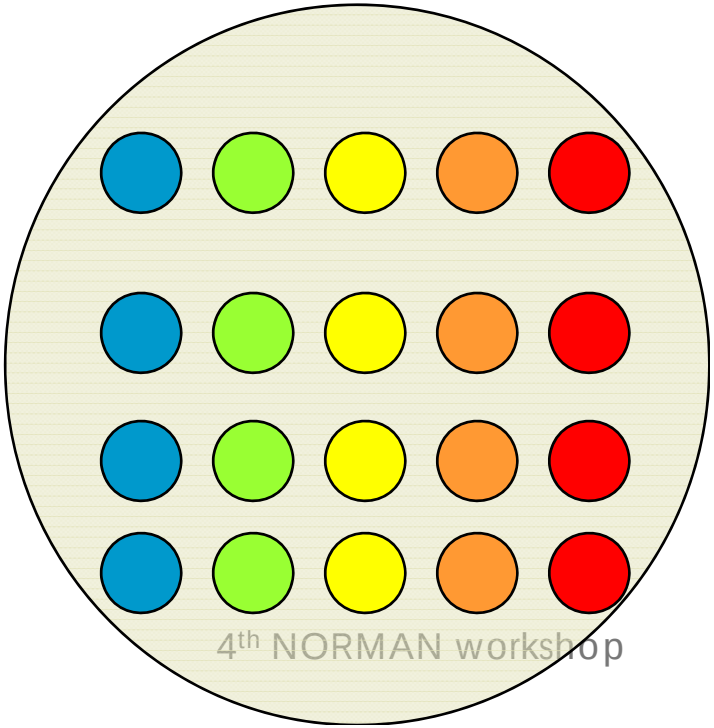
Synthetic indices

GENERIC ASSESSMENT FRAMEWORKS (ICES, 2008)



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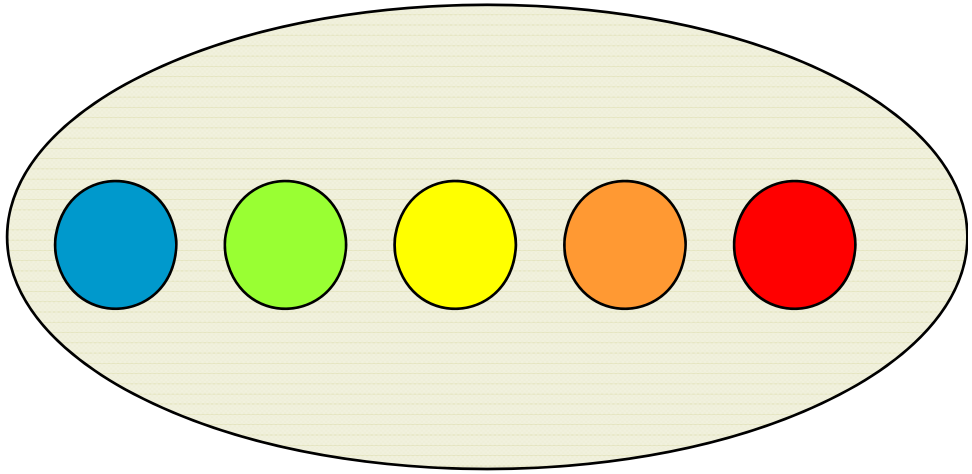

Merçi

Thank you

Gracias