



# DGTs, A COMPLEMENTARY TOOL TOWARDS MORE EFFICIENT BIOMONITORING PRACTICES

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A. Donnay, P. Lejeune,  
K. Das, S. Gobert.

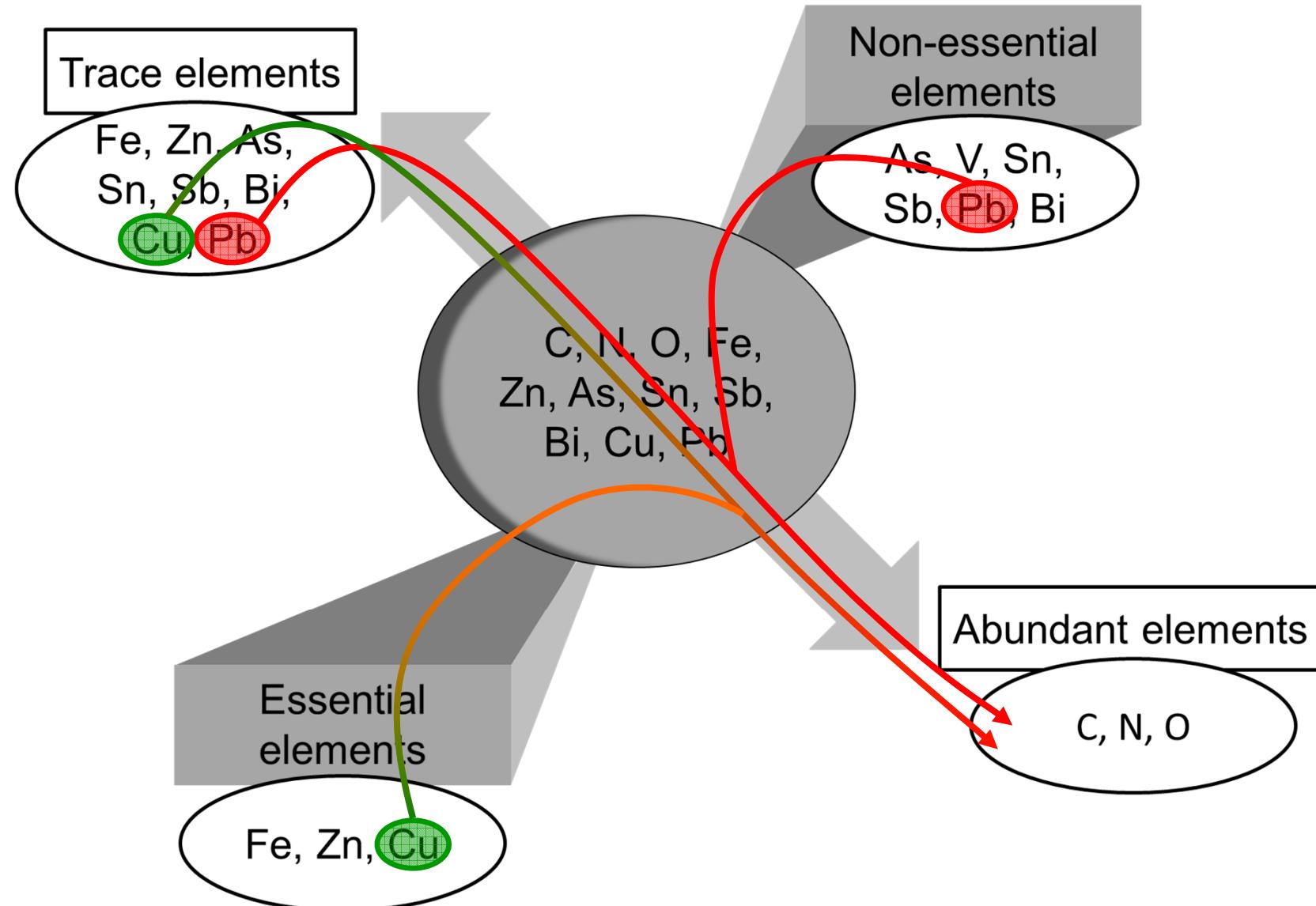
Donostia-San  
Sebastián  
01-10-15





# INTRODUCTION

## Trace elements



(after Amiard ,2011)

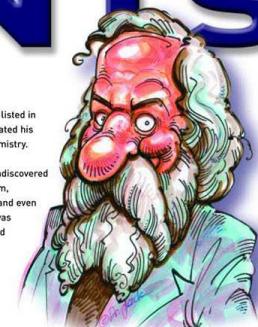


# PERIODIC TABLE of the ELEMENTS

ALKALI METALS  
ALKALI EARTH METALS  
TRANSITION METALS  
OTHER METALS  
OTHER NON-METALS  
HALOGENS  
NOBLE GASES  
RARE-EARTH METALS

H  
Hydrogen 1  
Symbol  
Element name  
Atomic number  
Atomic mass

**DMITRI MENDELEYEV (1834 – 1907)**  
The Russian chemist, Dmitri Mendeleev, was the first to observe that if elements were listed in order of atomic mass, they showed regular (periodical) repeating properties. He formulated his discovery in a periodic table of elements, now regarded as the backbone of modern chemistry.  
  
The crowning achievement of Mendeleev's periodic table lay in his prophecy of then, undiscovered elements. In 1869, the year he published his periodic classification, the elements gallium, germanium and scandium were unknown. Mendeleev left spaces for them in his table and even predicted their atomic masses and other chemical properties. Six years later, gallium was discovered and his predictions were found to be accurate. Other discoveries followed and their chemical behaviour matched that predicted by Mendeleev.  
  
This remarkable man, the youngest in a family of 17 children, has left the scientific community with a classification system so powerful that it became the cornerstone in chemistry teaching and the prediction of new elements ever since.  
In 1955, element 101 was named after him: Md, Mendelevium.



1 IA H Hydrogen 1 1.01	2 IIA Li Lithium 3 6.94	3 IIA Be Beryllium 4 9.01	18 VIIA He Helium 2 4.00
2 IA Na Sodium 11 22.99	2 IIA Mg Magnesium 12 24.31	13 IIIA C Carbon 6 12.01	17 VIIA F Fluorine 9 19.00
3 IA K Potassium 19 39.10	3 IIA Ca Calcium 20 40.08	14 IVA B Boron 5 10.81	16 VIA N Nitrogen 7 14.01
4 IA Rb Rubidium 37 85.47	4 IIA Sr Strontium 38 87.62	15 VA Al Aluminium 13 26.98	15 VIIA O Oxygen 8 16.00
5 IA Cs Caesium 55 132.91	5 IIA Ba Barium 56 137.33	16 VI A Si Silicon 14 28.09	14 VIA S Sulphur 16 32.06
6 IA Fr Francium 87 (223)	Actinide Series	17 VIIA Cl Chlorine 17 35.45	13 VIIA Ar Argon 18 39.95
7 IA Ra Radium 88 (226)	Rf Rutherfordium 104 (261)	18 IIIA Ga Germanium 31 69.72	Kr Krypton 36 83.80
8 IA	Db Dubnium 105 (262)	19 IV A Ge Germanium 32 72.61	Br Bromine 35 79.90
9 IA	Sg Seaborgium 106 (263)	20 V A As Arsenic 33 74.92	Iodine 53 126.90
10 IA	Bh Bohrium 107 (262)	21 VI A Sn Tin 50 118.71	Xe Xenon 54 131.29
11 IA	Hs Hassium 108 (265)	22 VIIA Te Tellurium 52 127.60	At Astatine 85 (210)
12 IA	Mt Meitnerium 109 (266)	23 IIIA Pb Lead 82 207.20	Rn Radon 86 (222)
13 IA	La Lanthanum 57 138.91	24 IV A Po Polonium 84 (209)	
14 IA	Ce Cerium 58 140.12	25 V A Bi Bismuth 83 208.98	
15 IA	Pr Praseodymium 59 140.90	26 VI A Tl Thallium 81 204.38	
16 IA	Nd Neodymium 60 144.24	27 VIIA Dy Dysprosium 66 162.50	
17 IA	Pm Promethium 61 (145)	28 IIIA Ho Holmium 67 164.93	
18 IA	Sm Samarium 62 150.36	29 IV A Er Erbium 68 167.26	
19 IA	Eu Europium 63 151.96	30 V A Tm Thulium 69 168.93	
20 IA	Gd Gadolinium 64 157.25	31 VI A Yb Yterbium 70 173.04	
21 IA	Tb Terbium 65 158.92	32 VIIA Lu Lutetium 71 174.96	
22 IA	Dy Dysprosium 66 162.50	33 IIIA Es Einsteinium 99 (256)	
23 IA	Ho Holmium 67 164.93	34 IV A Fm Fermium 100 (257)	
24 IA	Er Erbium 68 167.26	35 V A Md Mendelevium 101 (258)	
25 IA	Tm Thulium 69 168.93	36 VI A No Nobelium 102 (259)	
26 IA	Yb Yterbium 70 173.04	37 VIIA Lr Lawrencium 103 (260)	



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## Introduction



Ug

Direct measurements in water :

- ❖ low, punctual and fluctuating concentrations;
- ❖ preconcentrations;
- ❖ bioaccessible fraction?



Ecotoxicology :

bioindicators =  
organisms accumulating  
pollutants to levels  
representative of their  
habitat pollution status.



*Posidonia oceanica*



*Mytilus galloprovincialis*



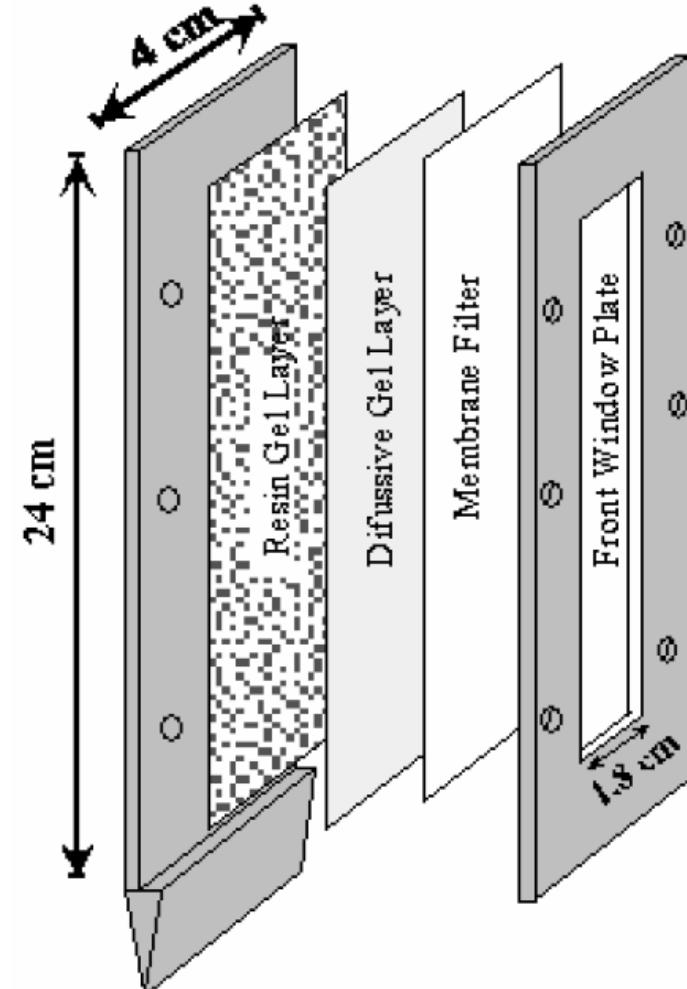
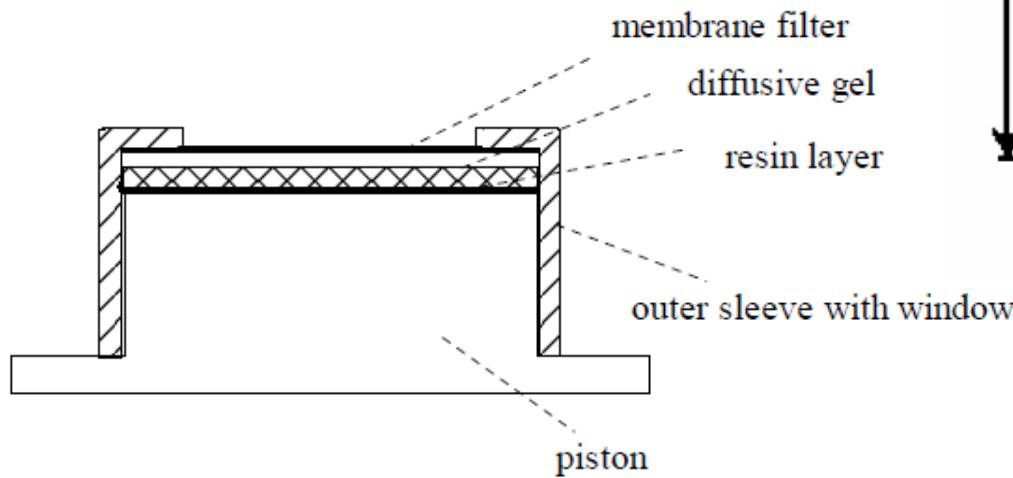


# INTRODUCTION

## Introduction

Davison and Zhang (1994).  
*In situ speciation measurements of trace components in natural waters using thin-film gels.*  
Nature. 367: 546-548.  
(Lancaster University, UK)

DGT = diffusive gradients in thin films



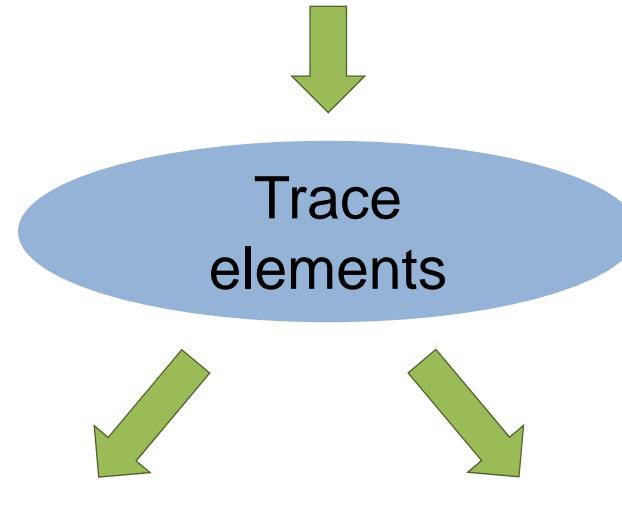
(DGT – for measurements in waters, soils and sediments)



# METHODS



## Monitoring



direct measurements in the environment:

- water
- sediment
- suspended matter



*Mytilus galloprovincialis*



*Posidonia oceanica*



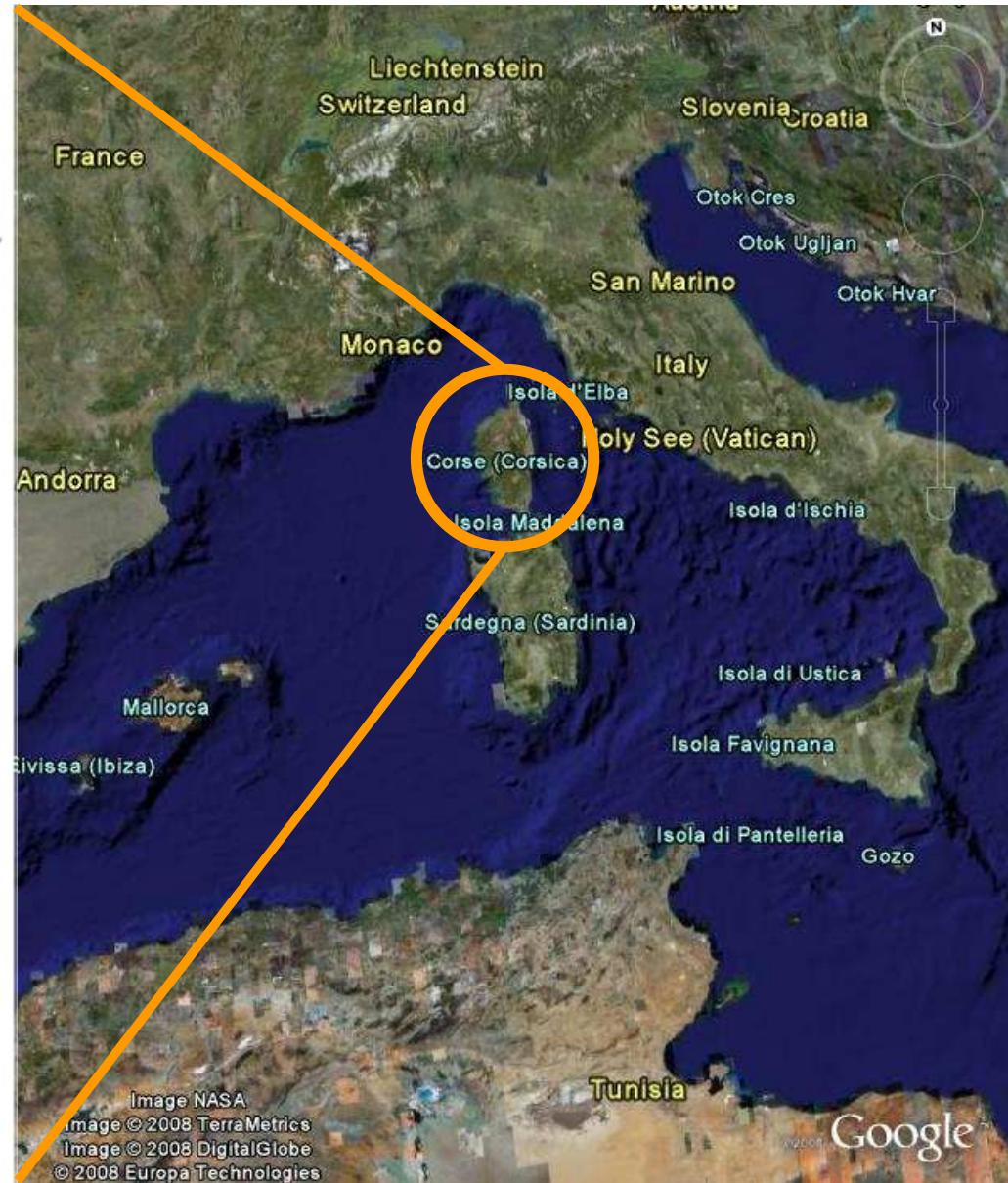
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## Calvi Bay

S  
I  
T  
E

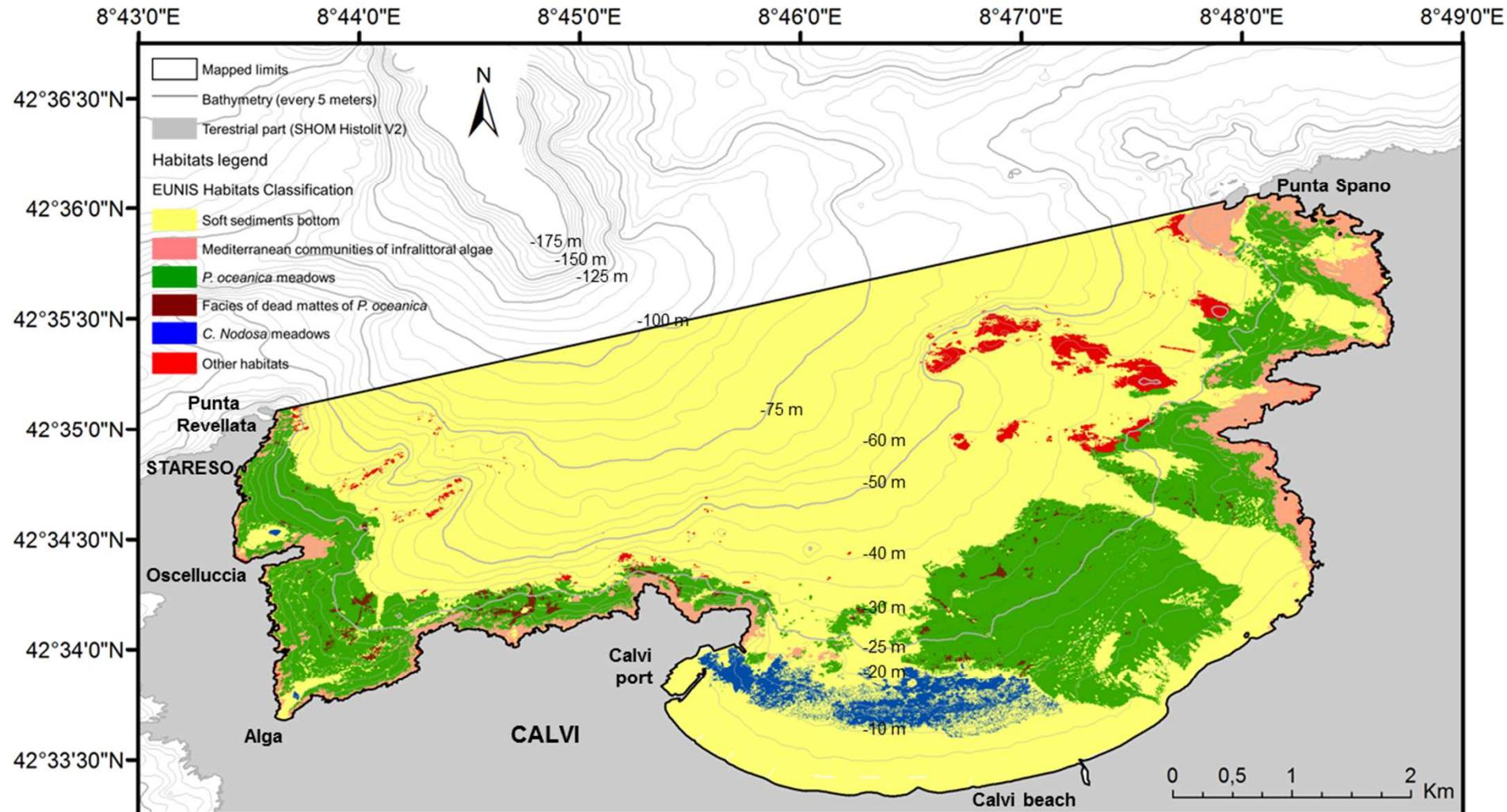




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# Calvi Bay



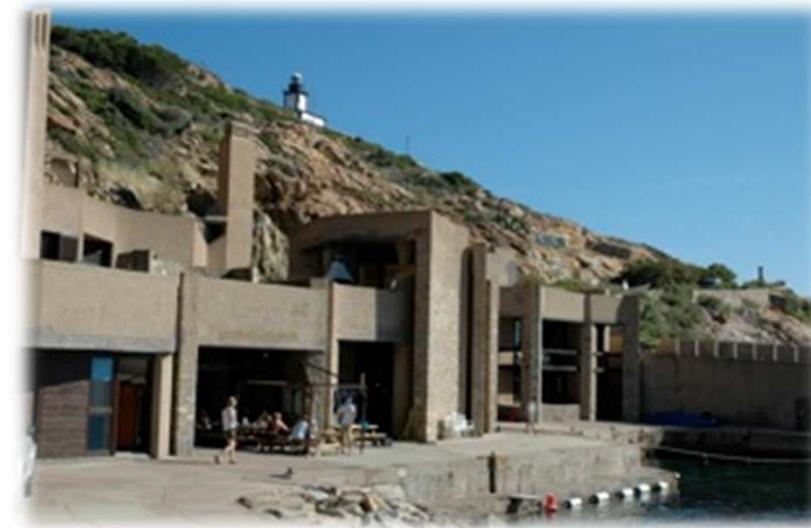
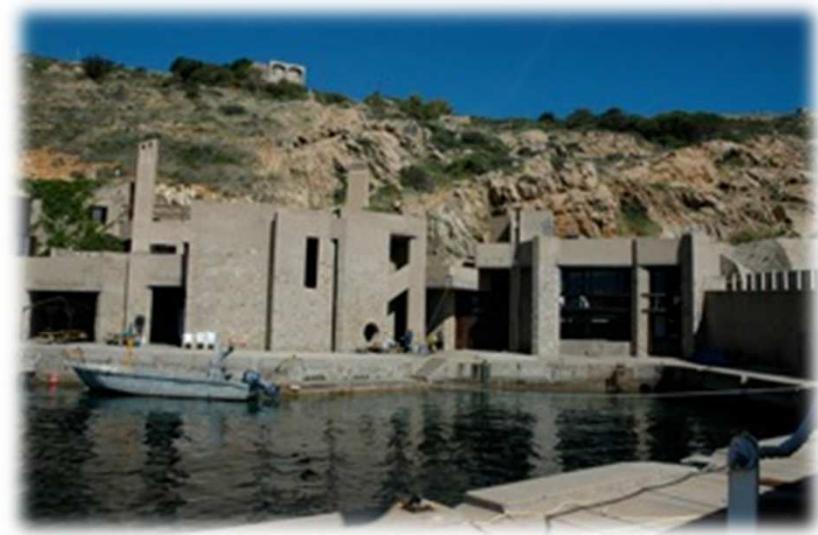
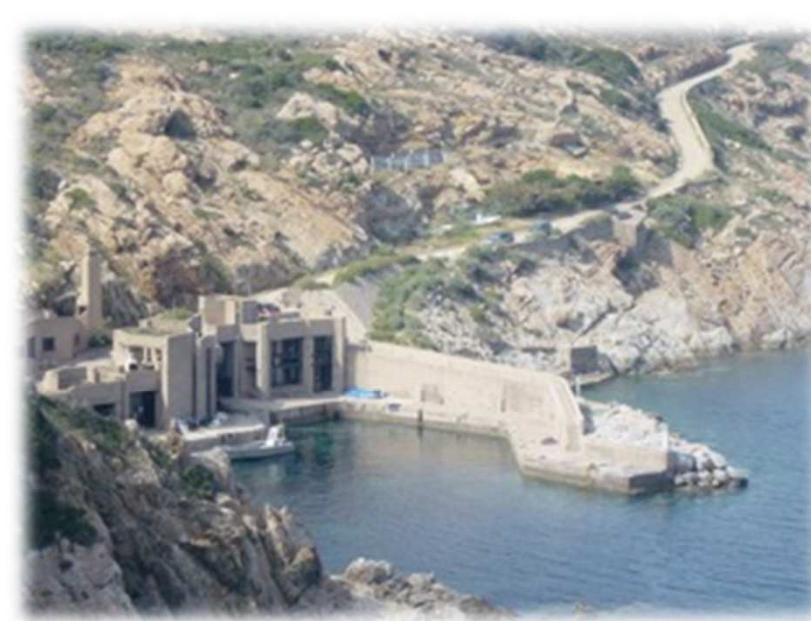


# STARESO

S  
I  
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E



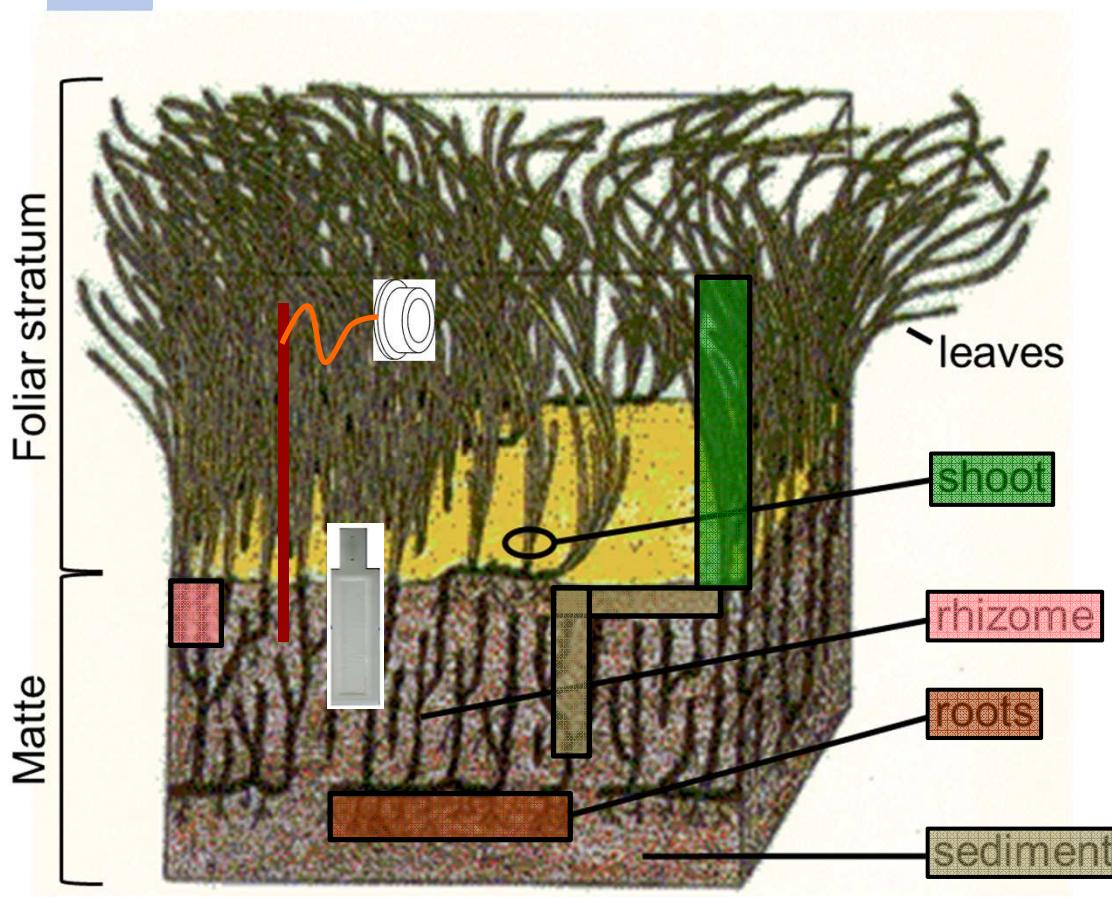
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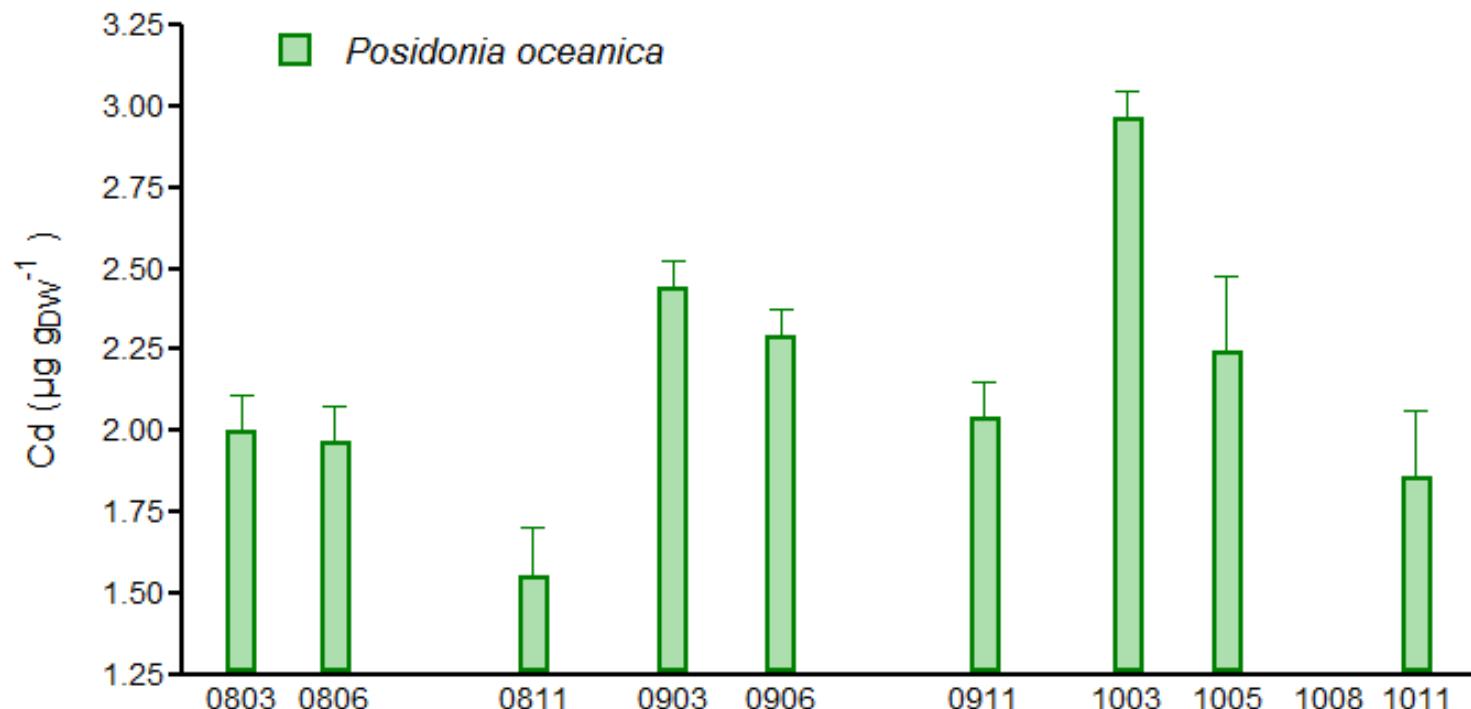


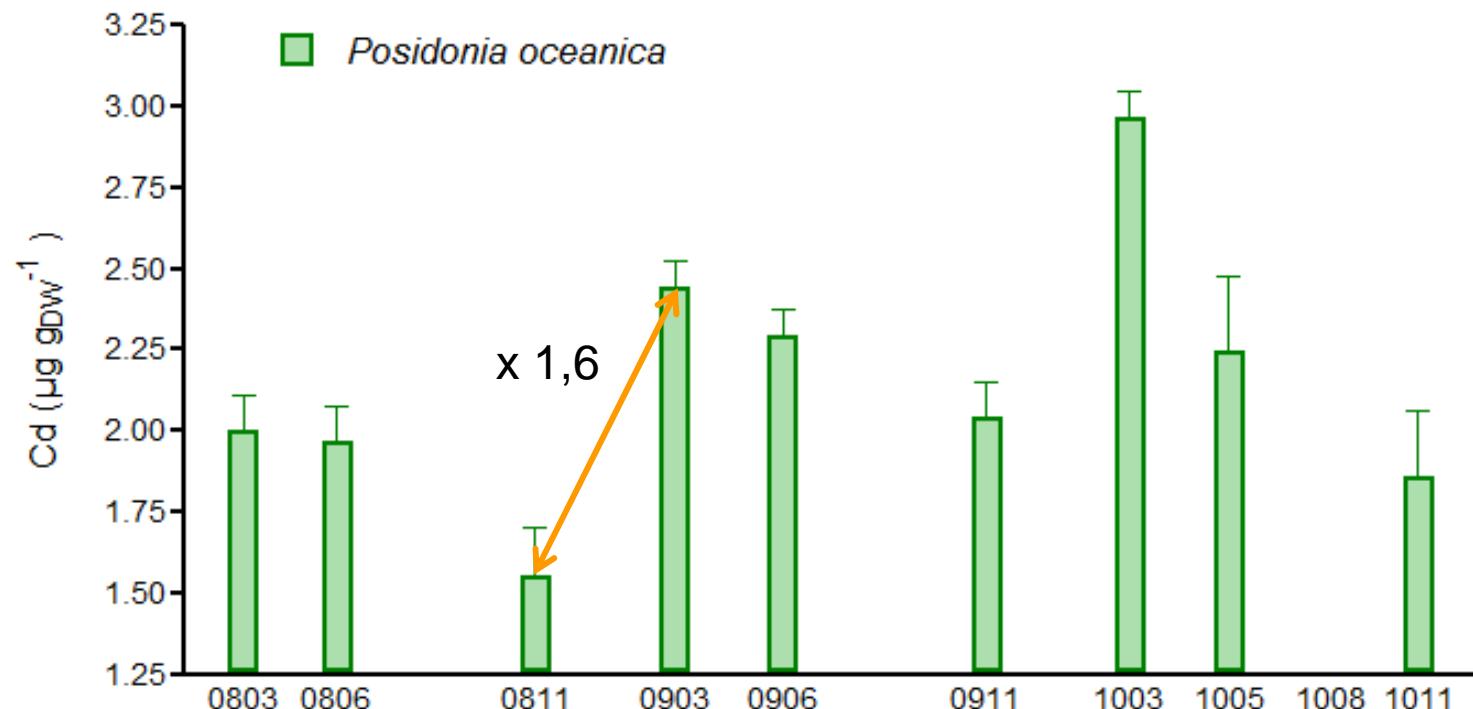
## *Posidonia oceanica*

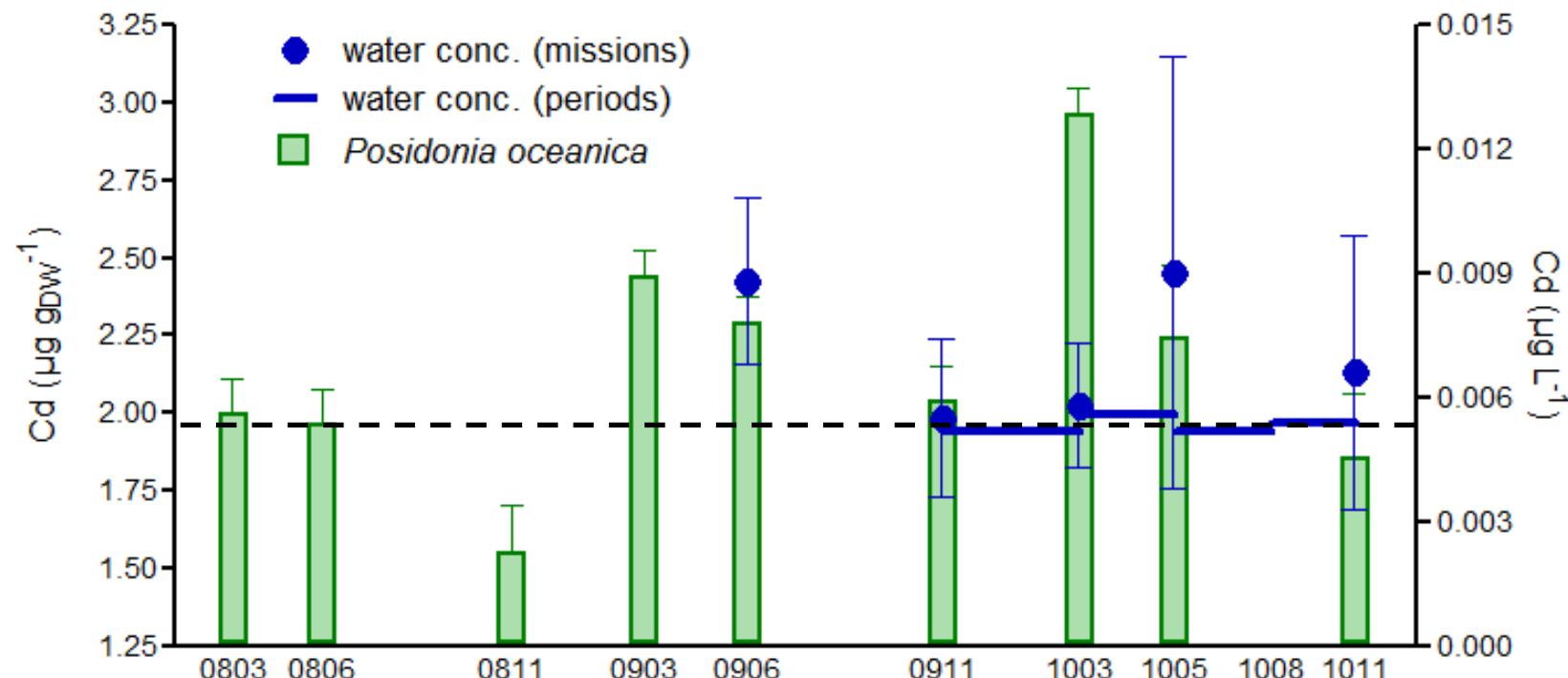
- ❖ *Posidonia oceanica*: shoots, rhizomes and roots;
- ❖ Foliar stratum;
- ❖ Matte.





Seasonal variations of *P. oceanica* [TE]A  
P  
P  
L  
I  
C  
A  
T  
I  
O  
N

Seasonal variations of *P. oceanica* [TE]A  
P  
P  
L  
I  
C  
A  
T  
I  
O  
N

Seasonal variations of *P. oceanica* [TE]A  
P  
P  
L  
I  
C  
A  
T  
I  
O  
N  
1[Cd] *Posidonia oceanica* :  $10^6$  times > water

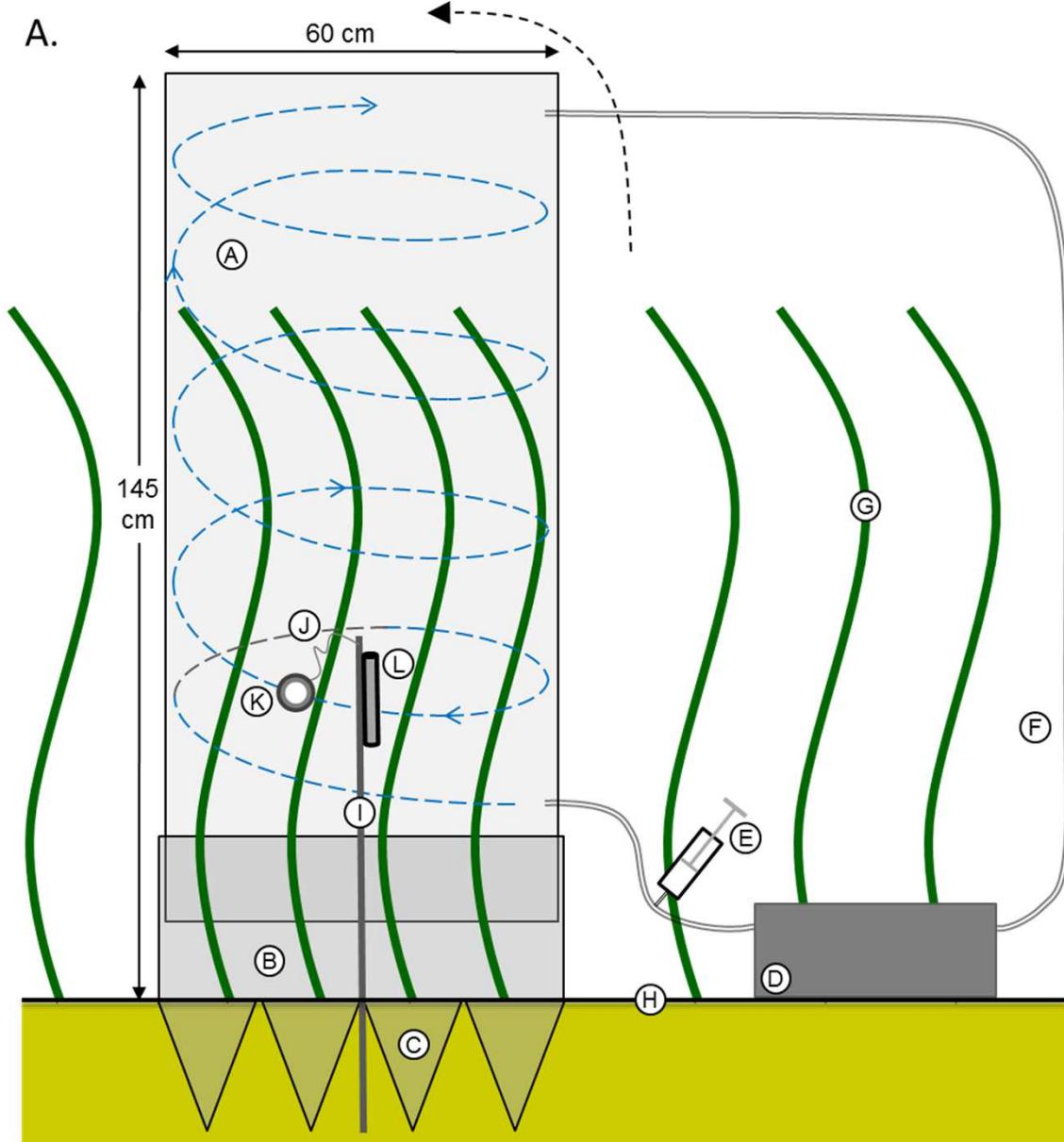


## In situ contamination of *P. oceanica*

### APPLICATION

2

- 5 days of contamination;
- 15 TEs (Pb, Co, Ag, Al, Mn ...);
- 410L bell-shaped mesocosm;
- Contamination every 12 hours (9am-9pm);
- 15 days of decontamination.







## In situ contamination of *P. oceanica*

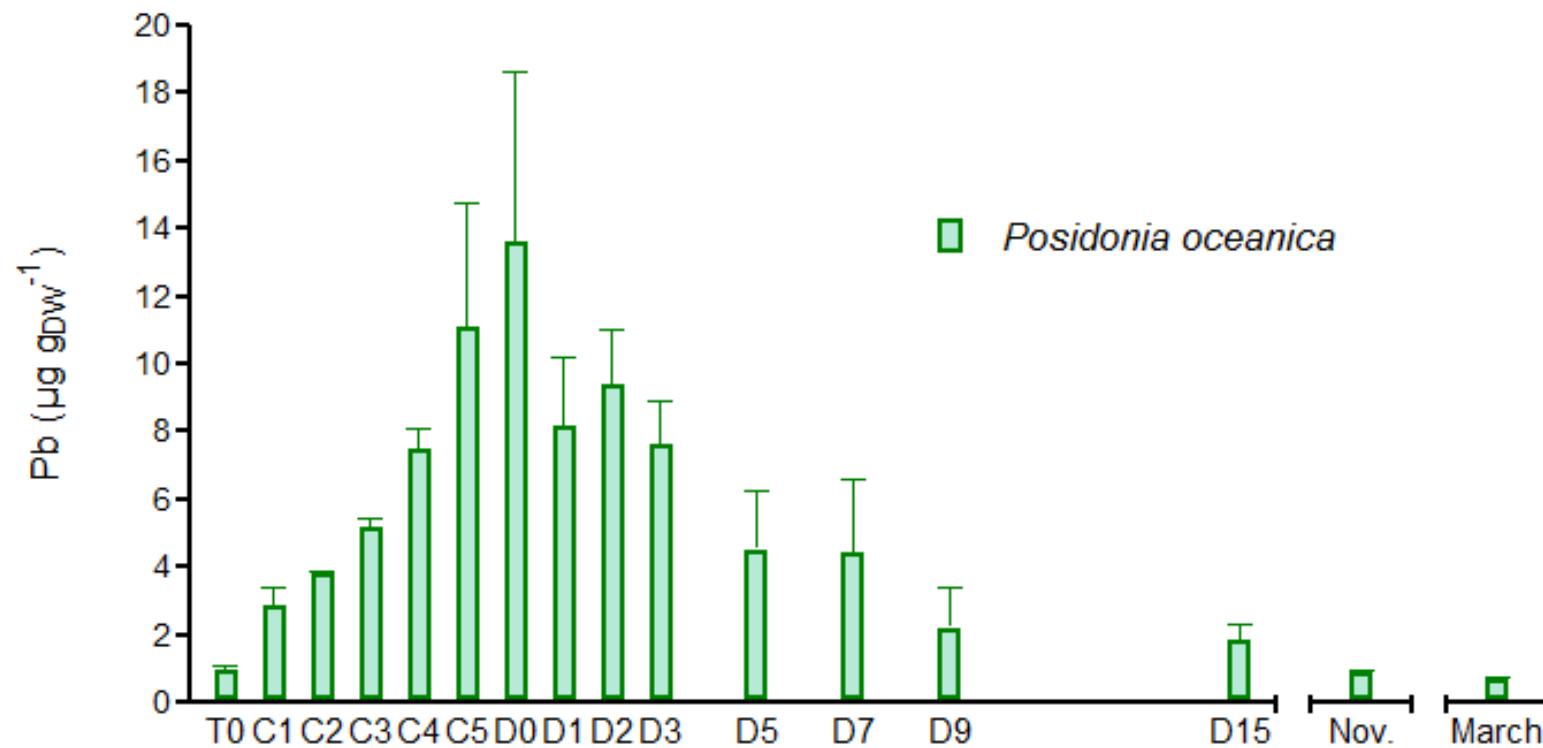
A  
P  
P  
L  
I  
C  
A  
T  
I  
O  
N

2



seawater average [Pb] :  $0.13 \mu\text{g L}^{-1}$

contamination level :  $5 \mu\text{g L}^{-1}$





# A P P L I C A T I O N

2



## *In situ* contamination of *P. oceanica*

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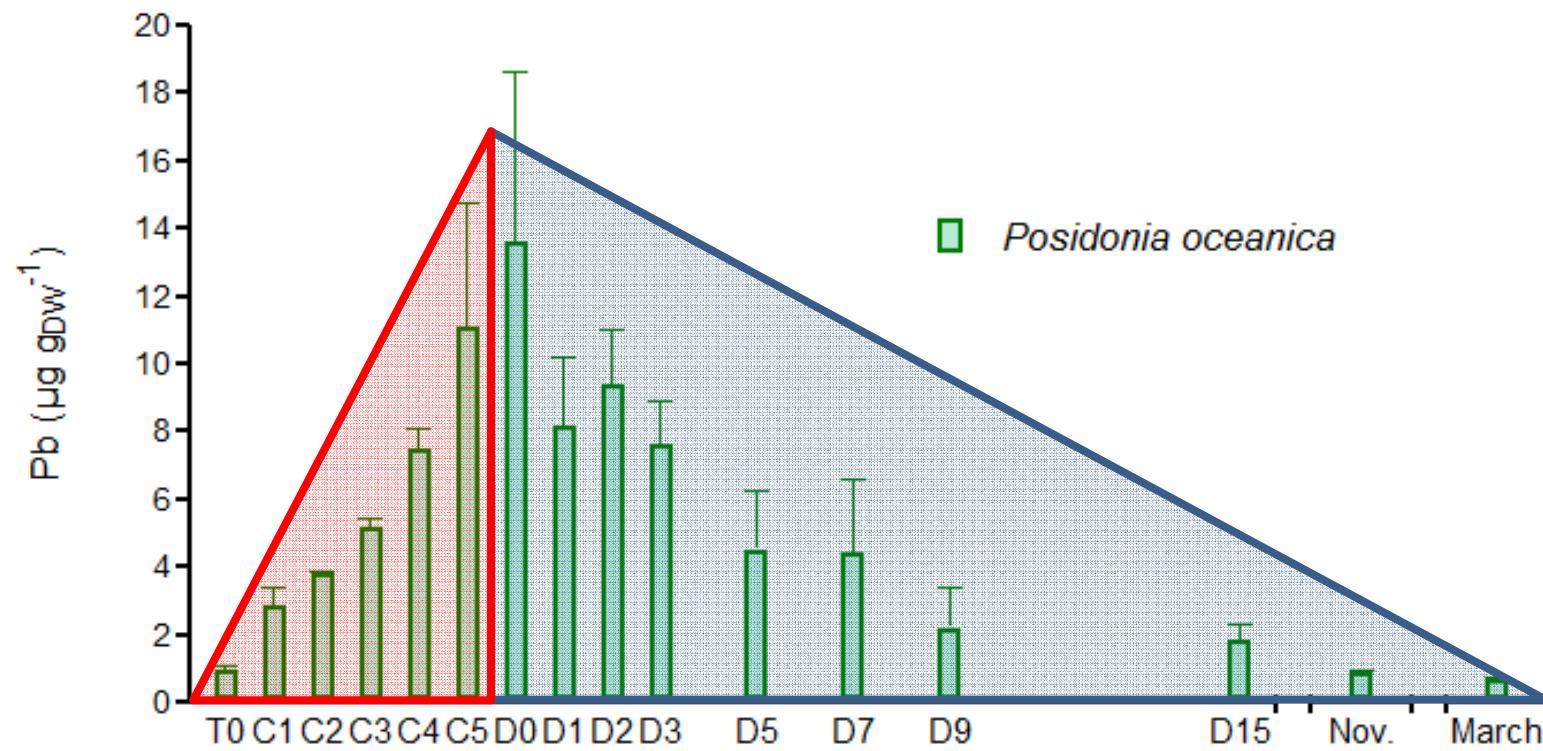


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contamination level :  $5 \mu\text{g L}^{-1}$

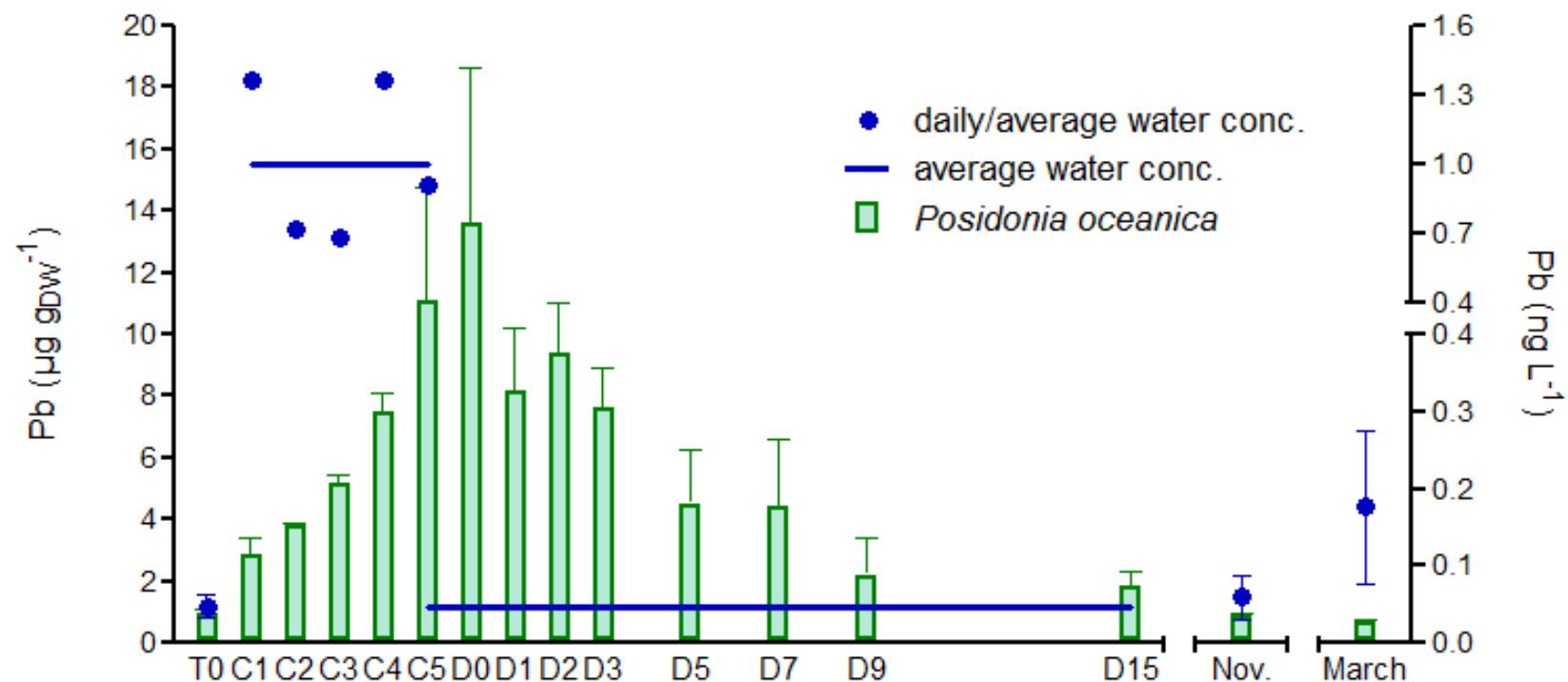




## In situ contamination of *P. oceanica*

A  
P  
P  
L  
I  
C  
A  
T  
I  
O  
N

2



seawater average [Pb] :  $0.05 \mu\text{g L}^{-1}$  ( $0.13 \mu\text{g L}^{-1}$ )

contamination level :  $1.00 \mu\text{g L}^{-1}$  ( $5 \mu\text{g L}^{-1}$ )





## In situ contamination of *P. oceanica*

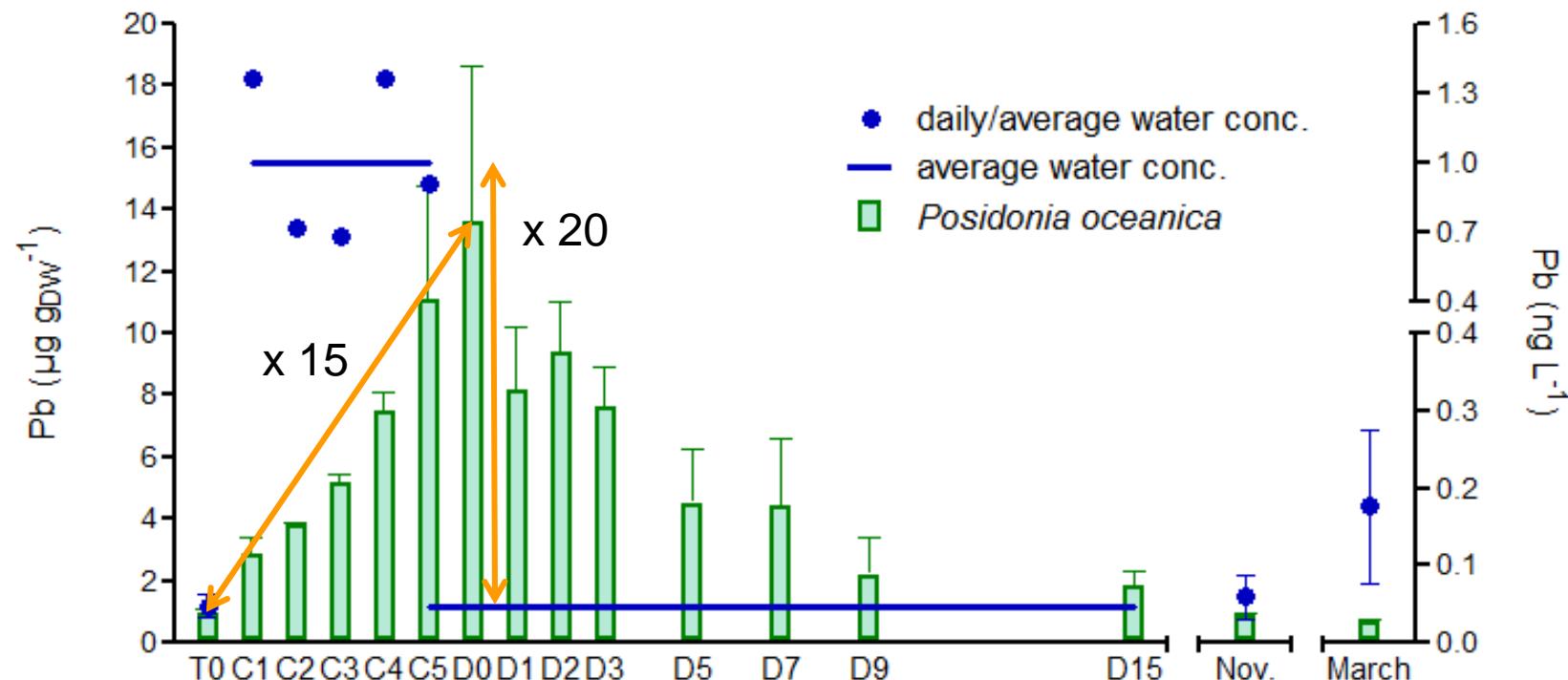
A  
P  
P  
L  
I  
C  
A  
T  
I  
O  
N

2



seawater average [Pb] :  $0.05 \mu\text{g L}^{-1}$  ( $0.13 \mu\text{g L}^{-1}$ )

contamination level :  $1.00 \mu\text{g L}^{-1}$  ( $5 \mu\text{g L}^{-1}$ )

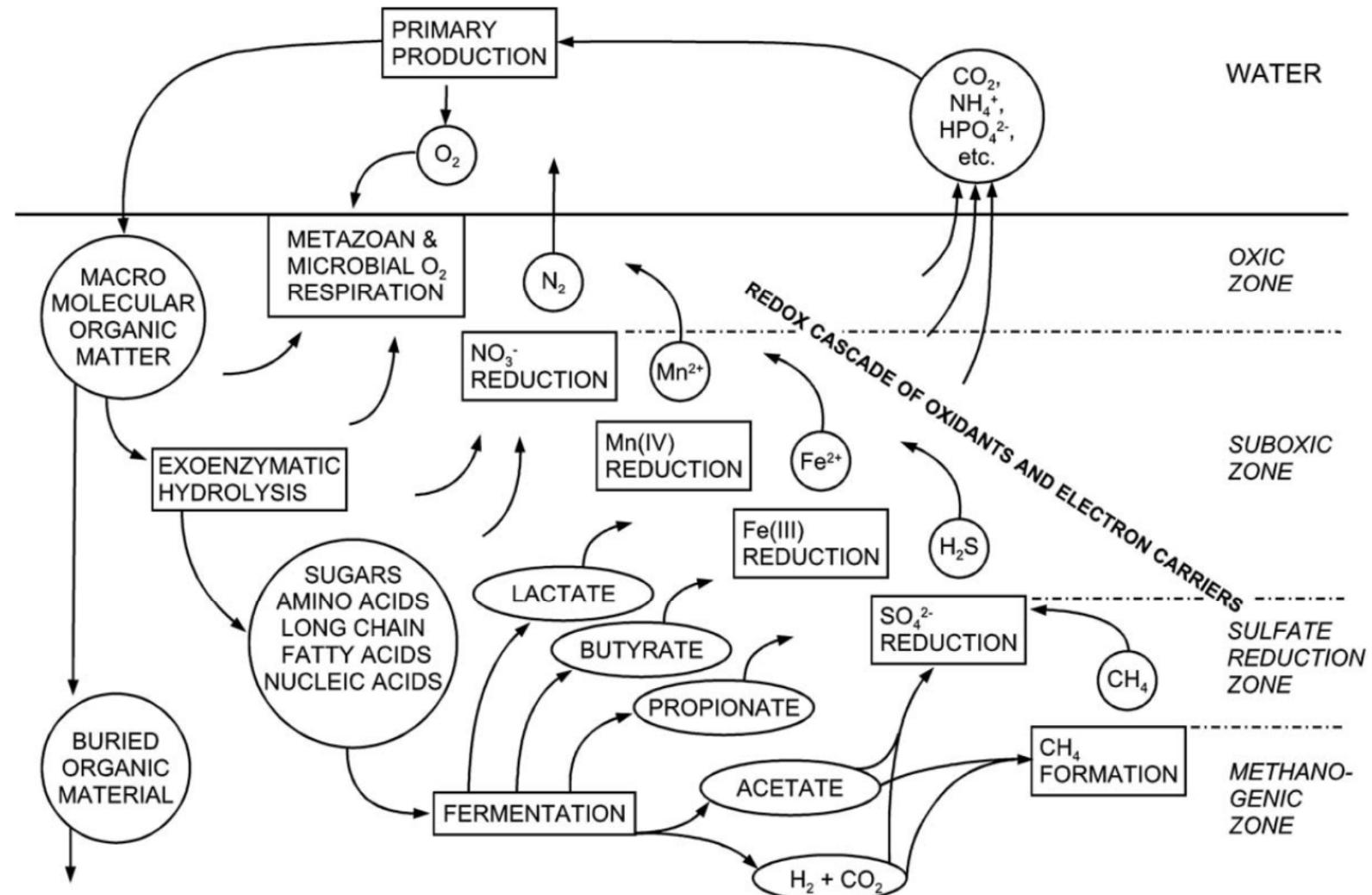




## Porewater TE concentrations

A  
P  
P  
L  
I  
C  
A  
T  
I  
O  
N

3



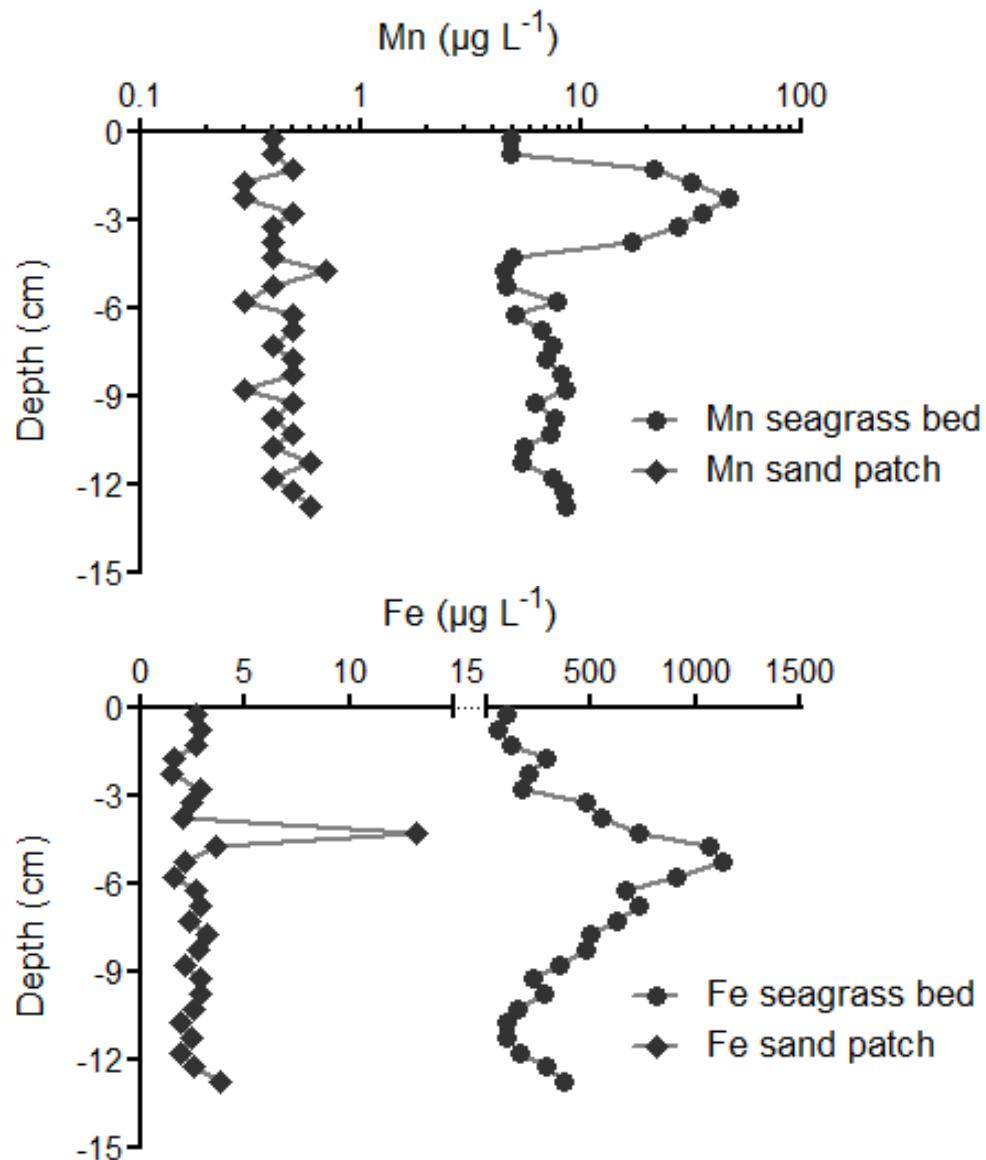
(Jørgensen, 2006)



# A P P L I C A T I O N

3  
Rem.: concentrations in the resin eluats after ICP-MS measurements.

## Porewater TE concentrations





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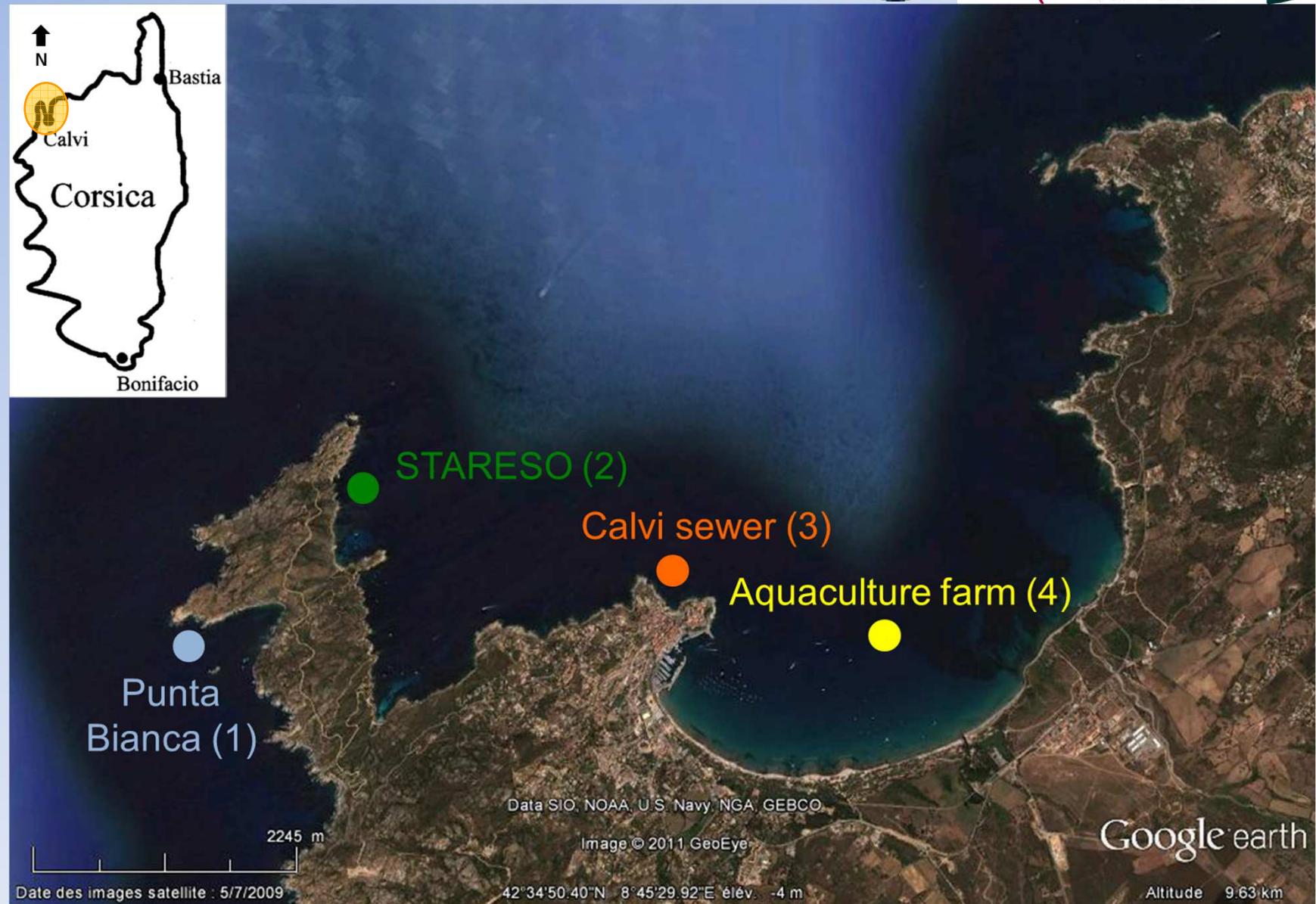
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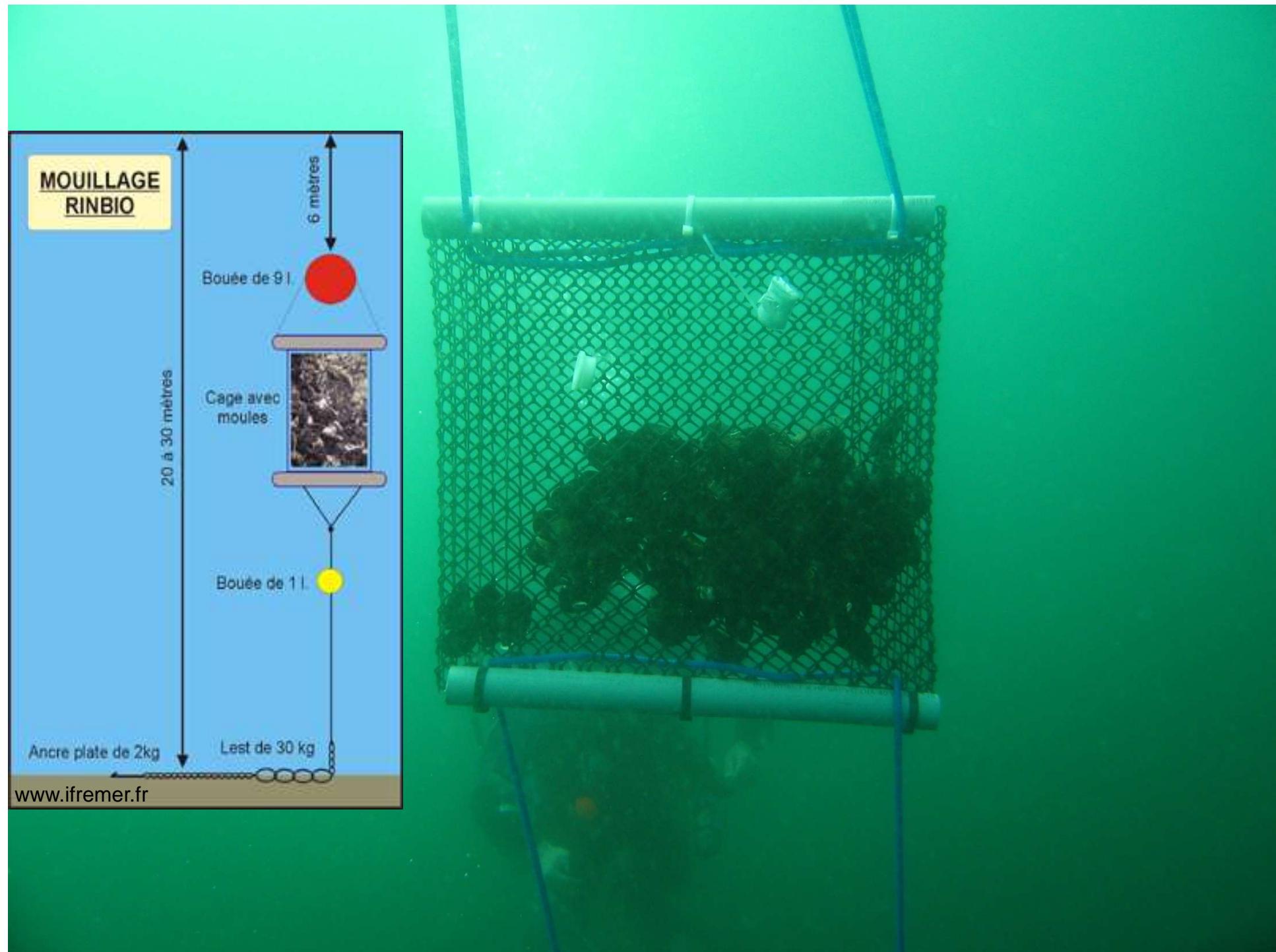


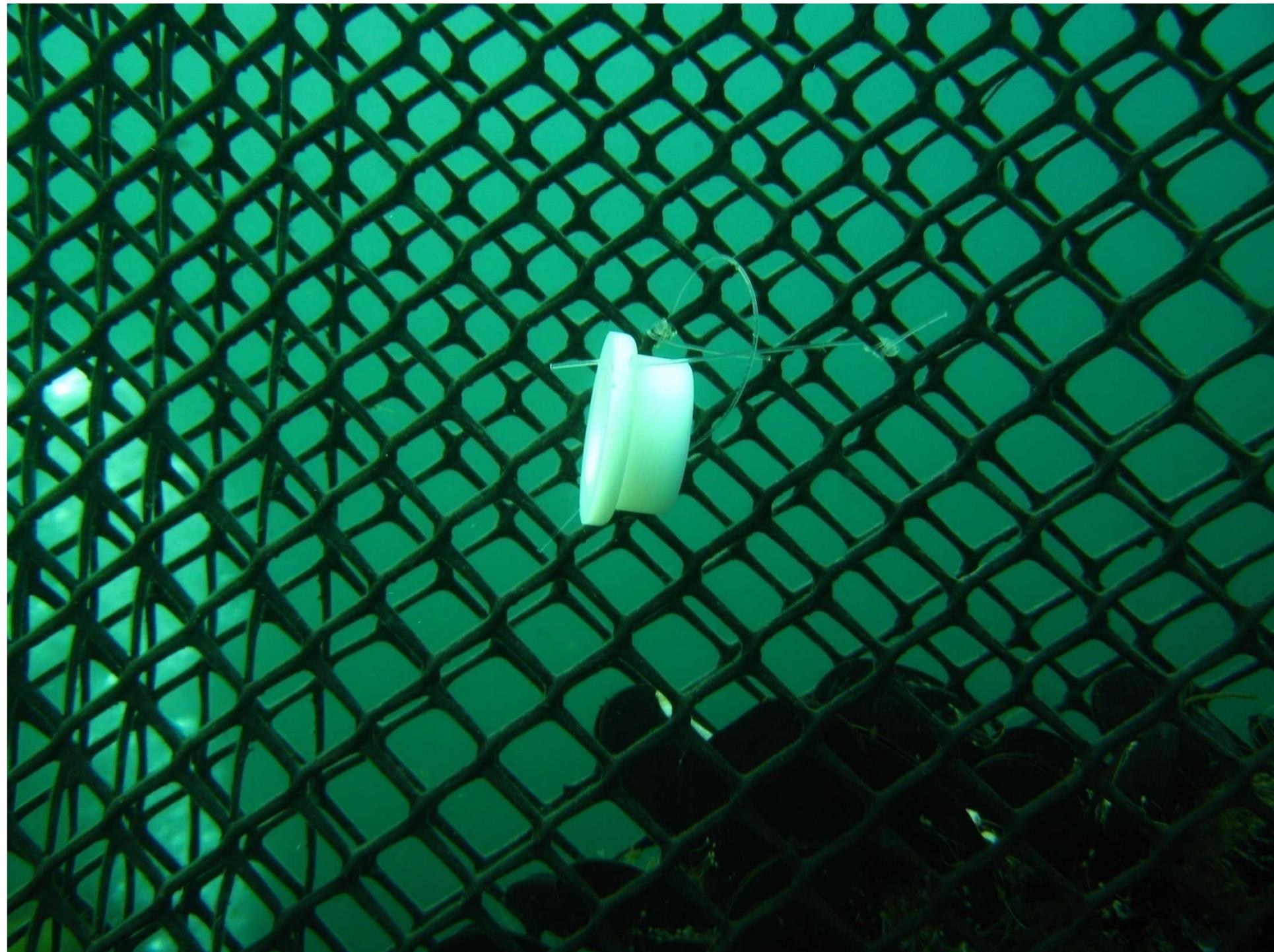
A  
P  
P  
L  
I  
C  
A  
T  
I  
O  
N



## Mussel caging: TE bioaccumulation







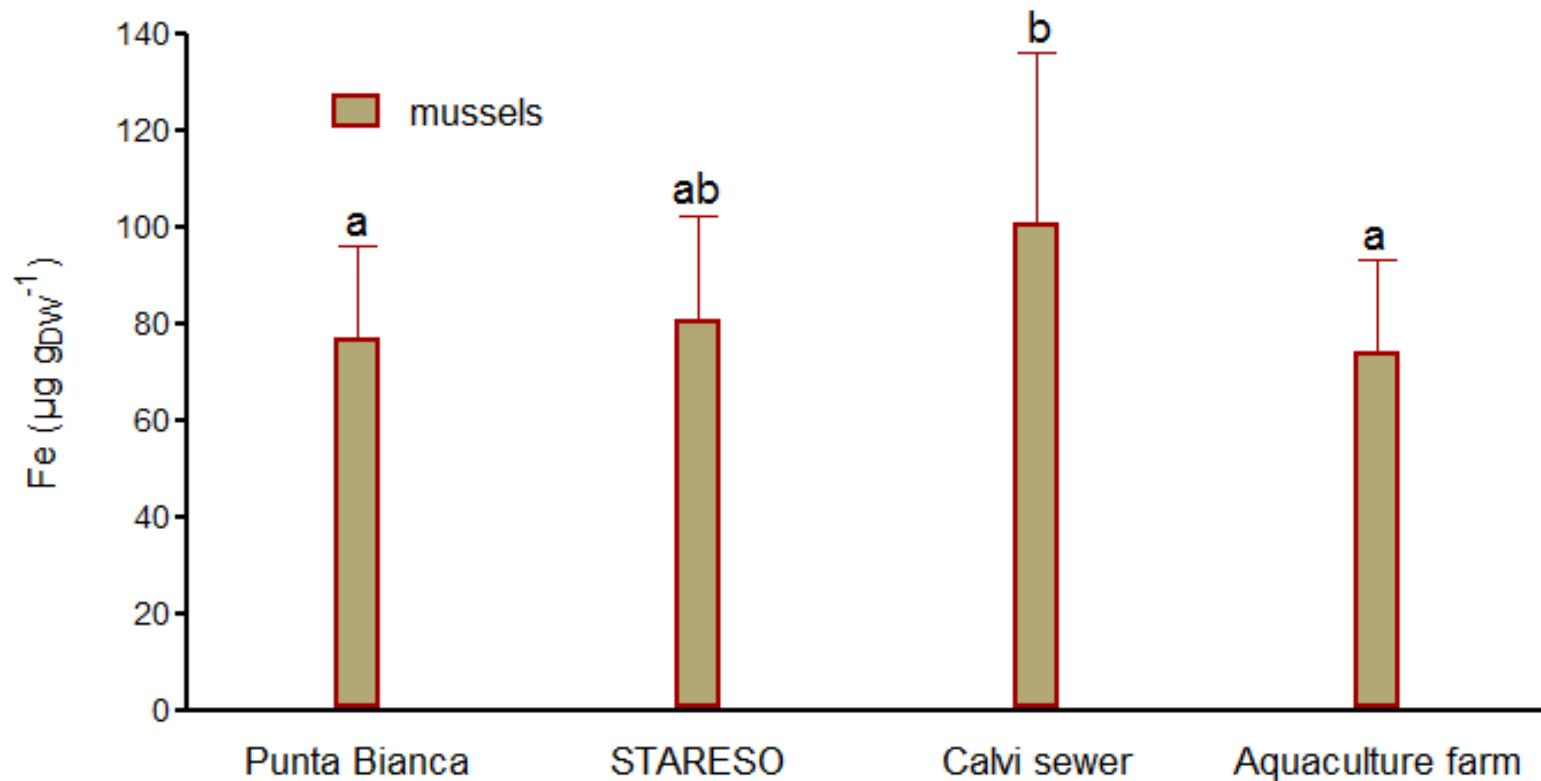


## Mussel caging: TE bioaccumulation

A  
P  
P  
L  
I  
C  
A  
T  
I  
O  
N

4

Calvi sewer / Aquaculture farm: mussels = 1.36

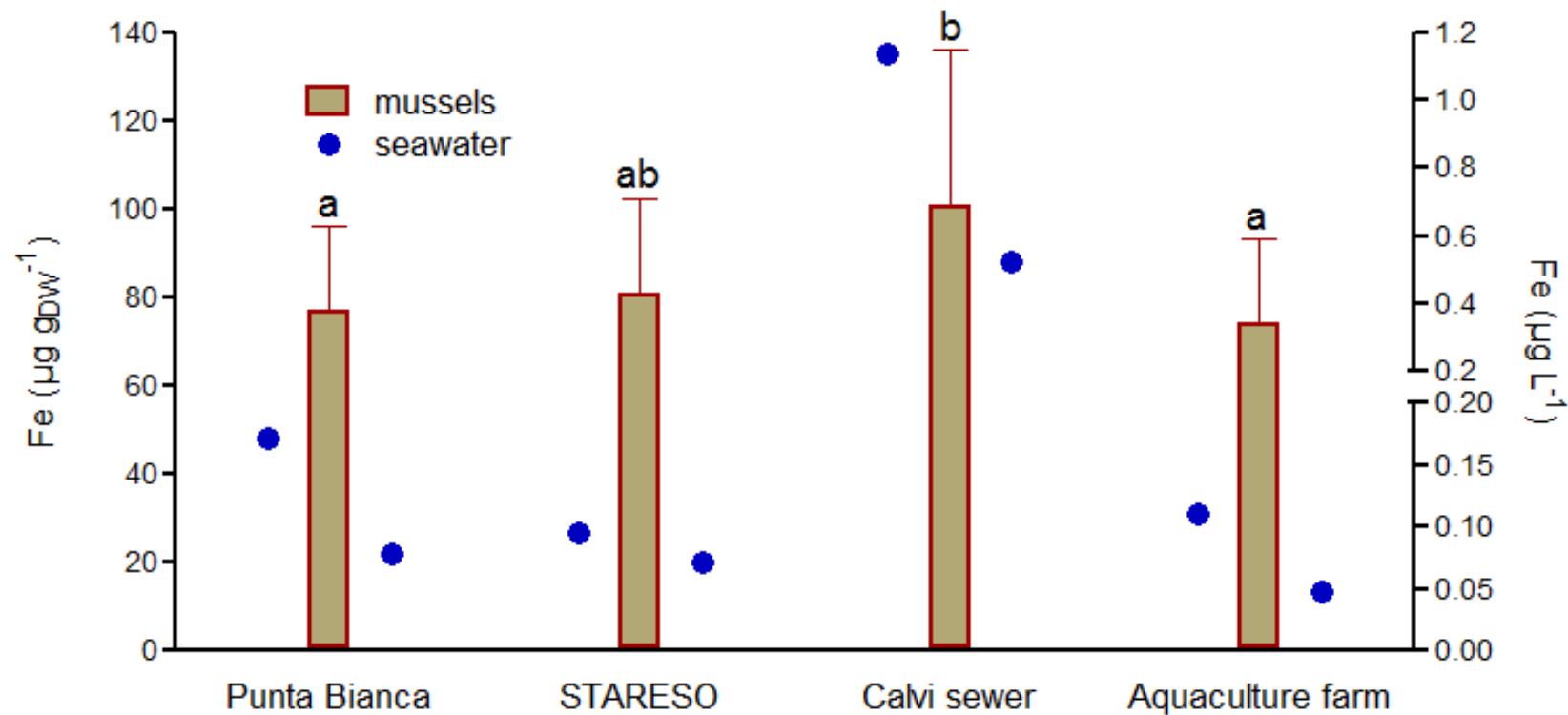




## Mussel caging: TE bioaccumulation

A  
P  
P  
L  
I  
C  
A  
T  
I  
O  
N

Calvi sewer / Aquaculture farm: mussels = 1.36

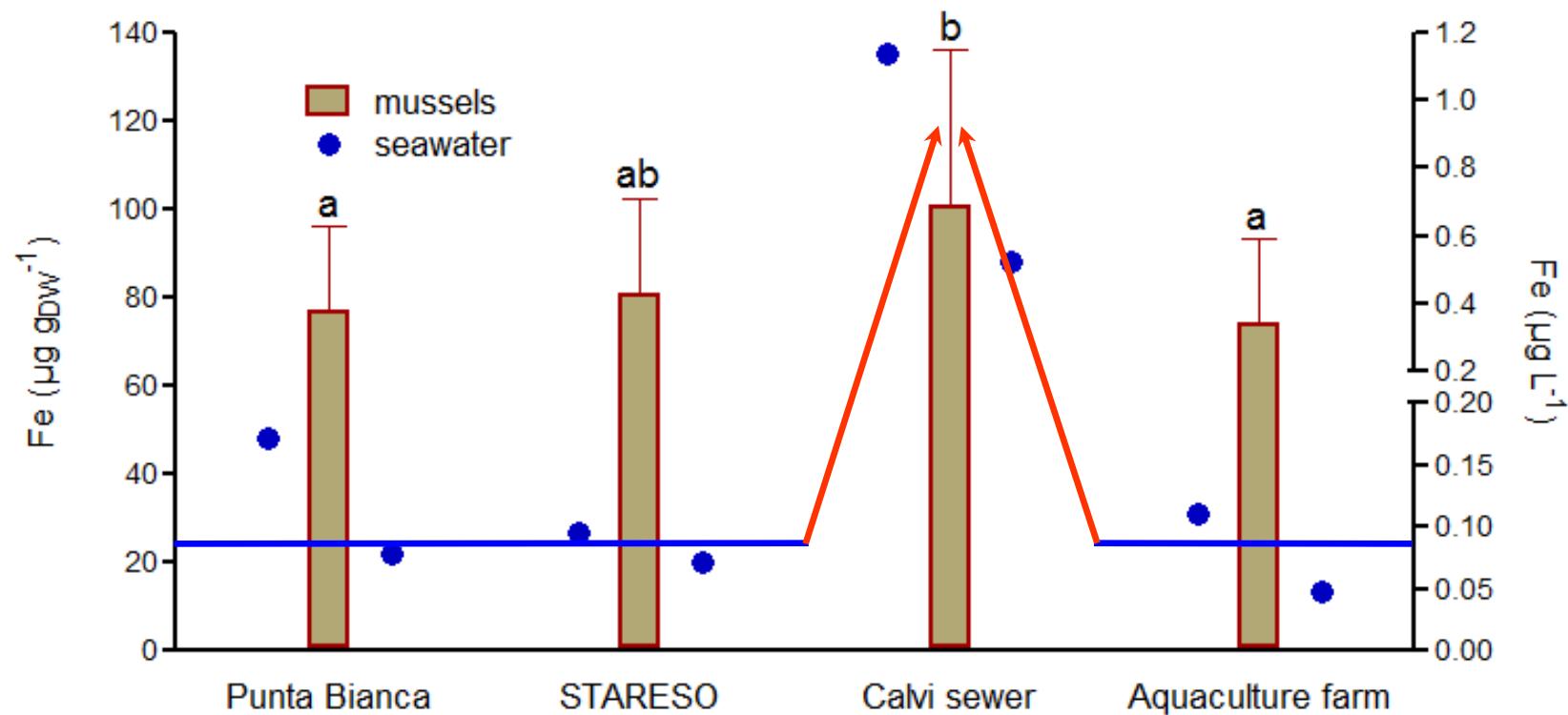




## Mussel caging: TE bioaccumulation

A  
P  
P  
L  
I  
C  
A  
T  
I  
O  
N

4

Calvi sewer / Aquaculture farm: mussels = 1.36  
water ~ 10

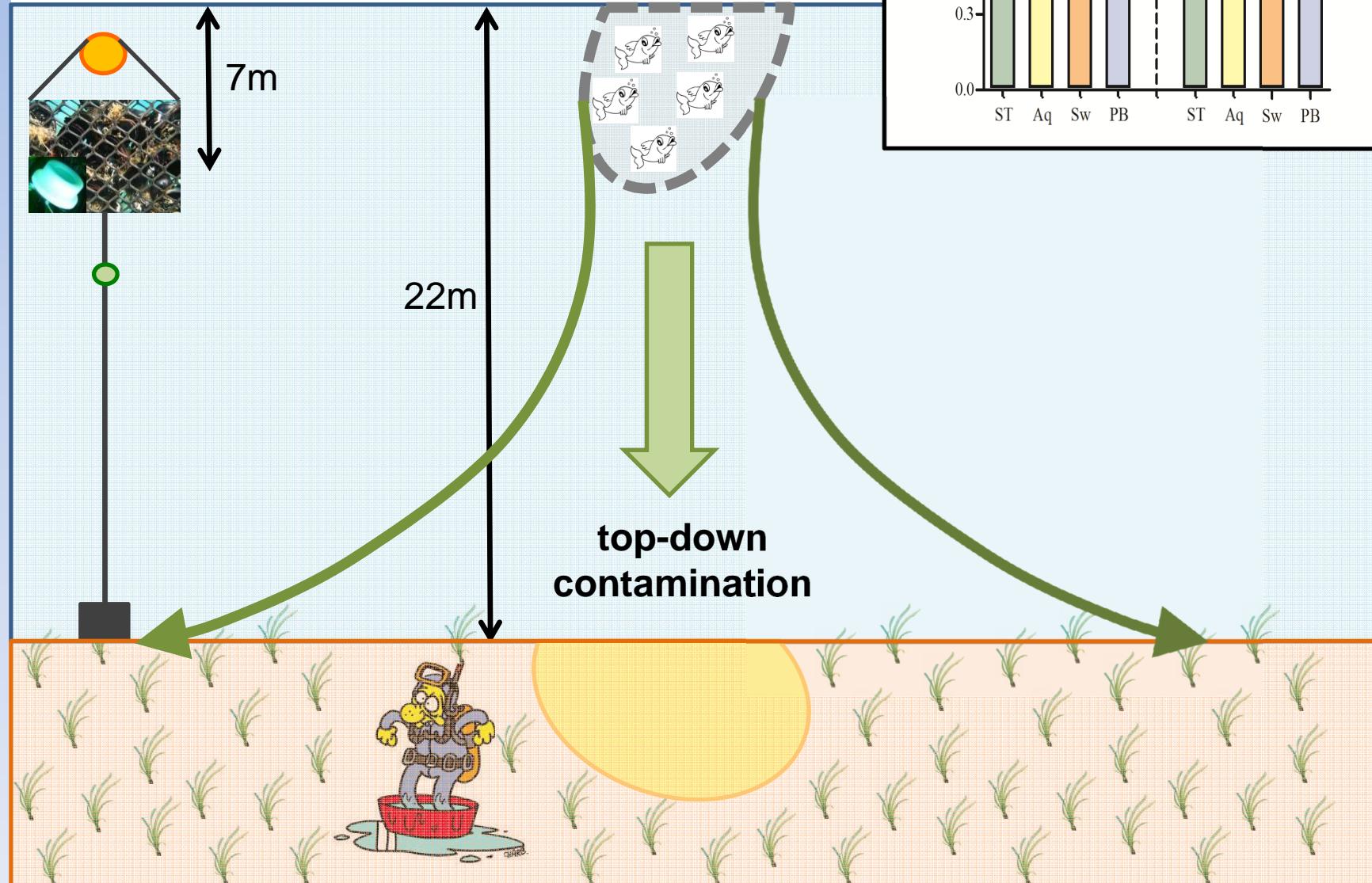


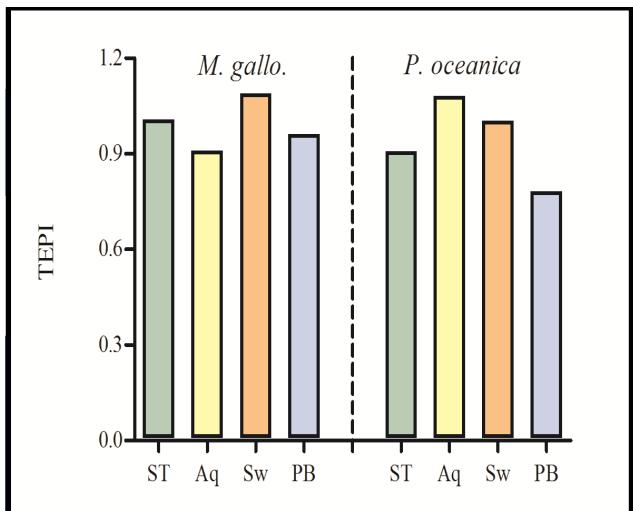
# A P P L I C A T I O N



## Mussel caging: TE bioaccumulation

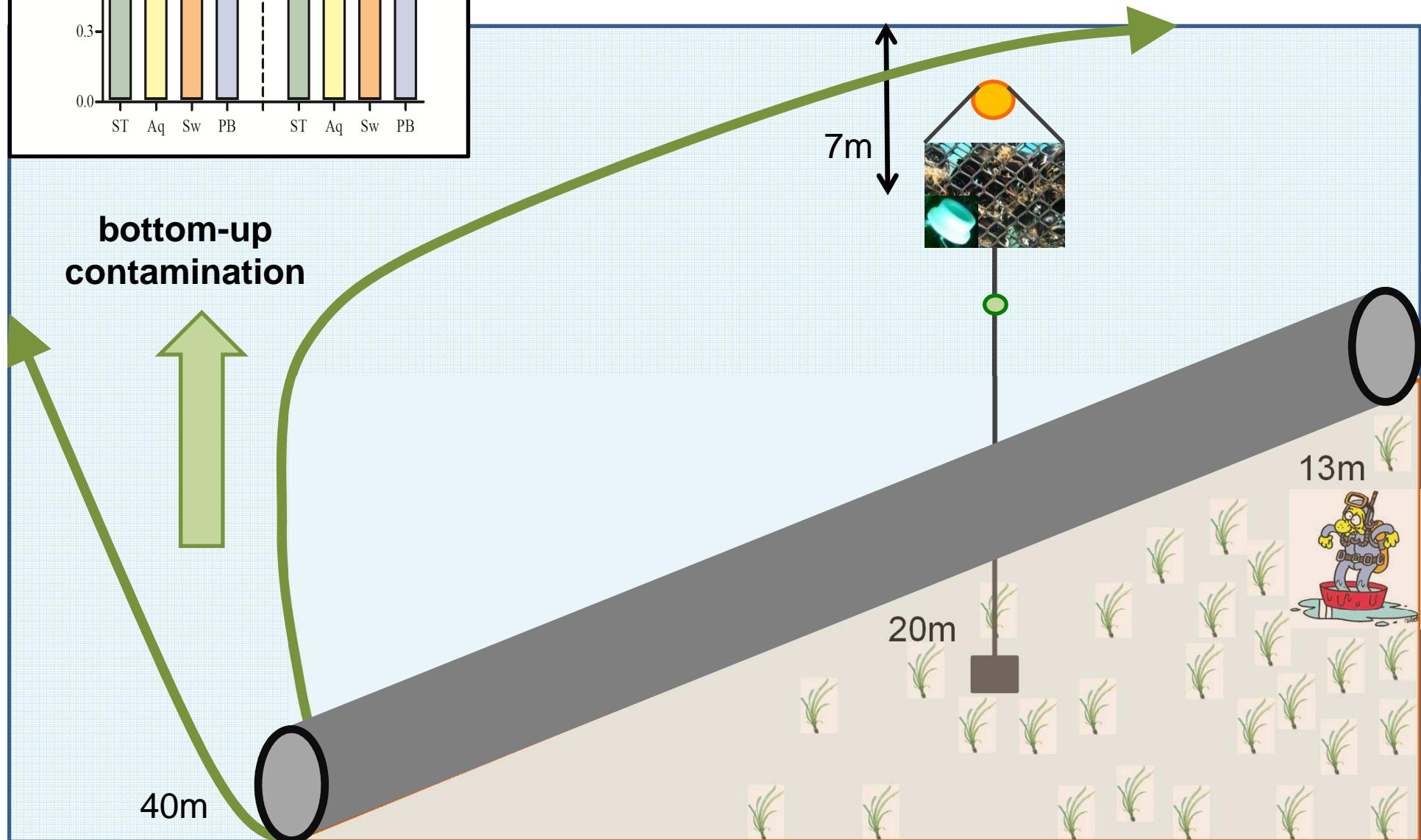
Calvi sewer / Aquaculture farm: mussels = 1.36





## Mussel caging: TE bioaccumulation

Calvi sewer / Aquaculture farm: mussels = 1.36





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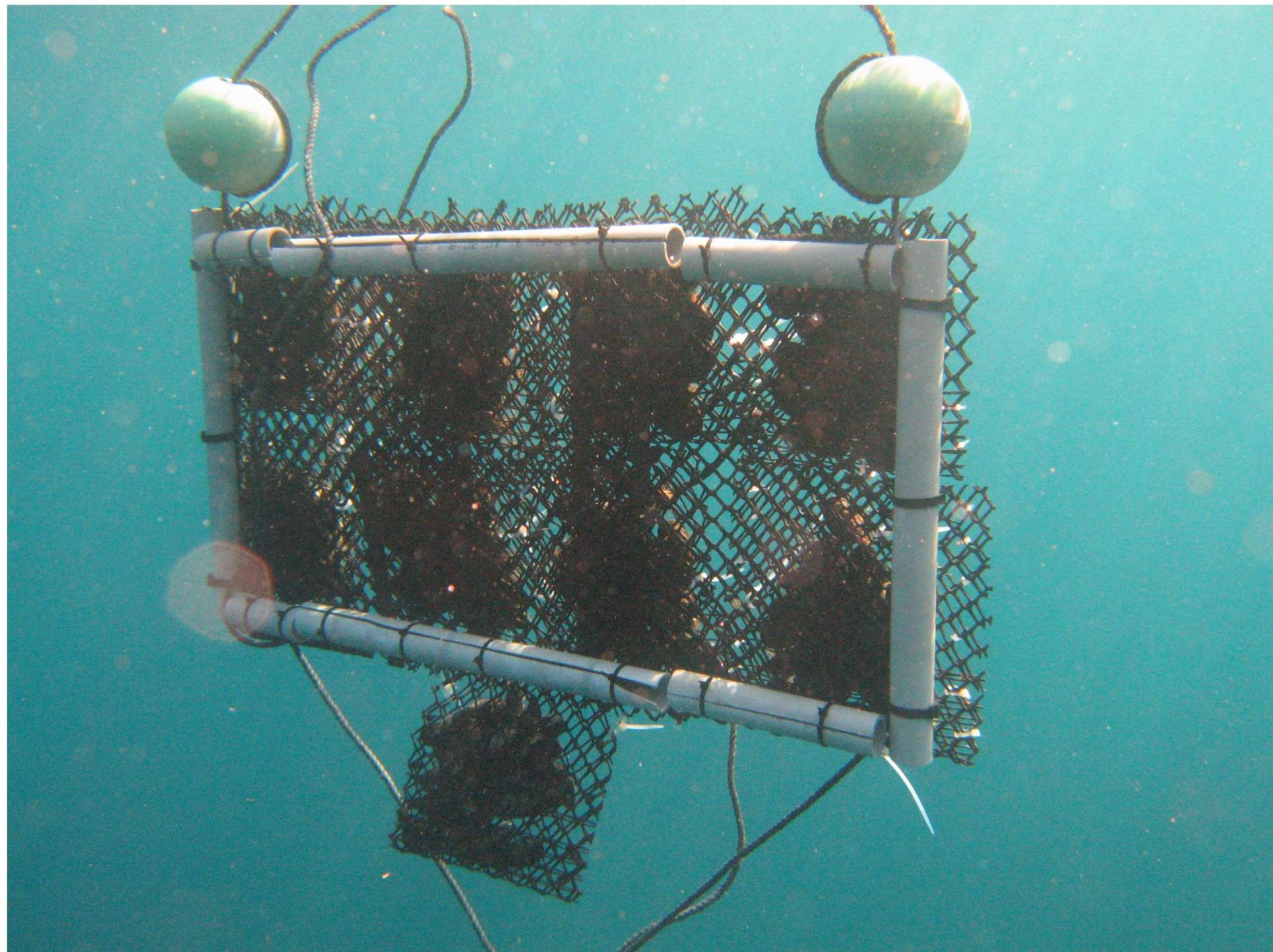


## TE kinetics in caged mussels

A  
P  
P  
L  
I  
C  
A  
T  
I  
O  
N

5



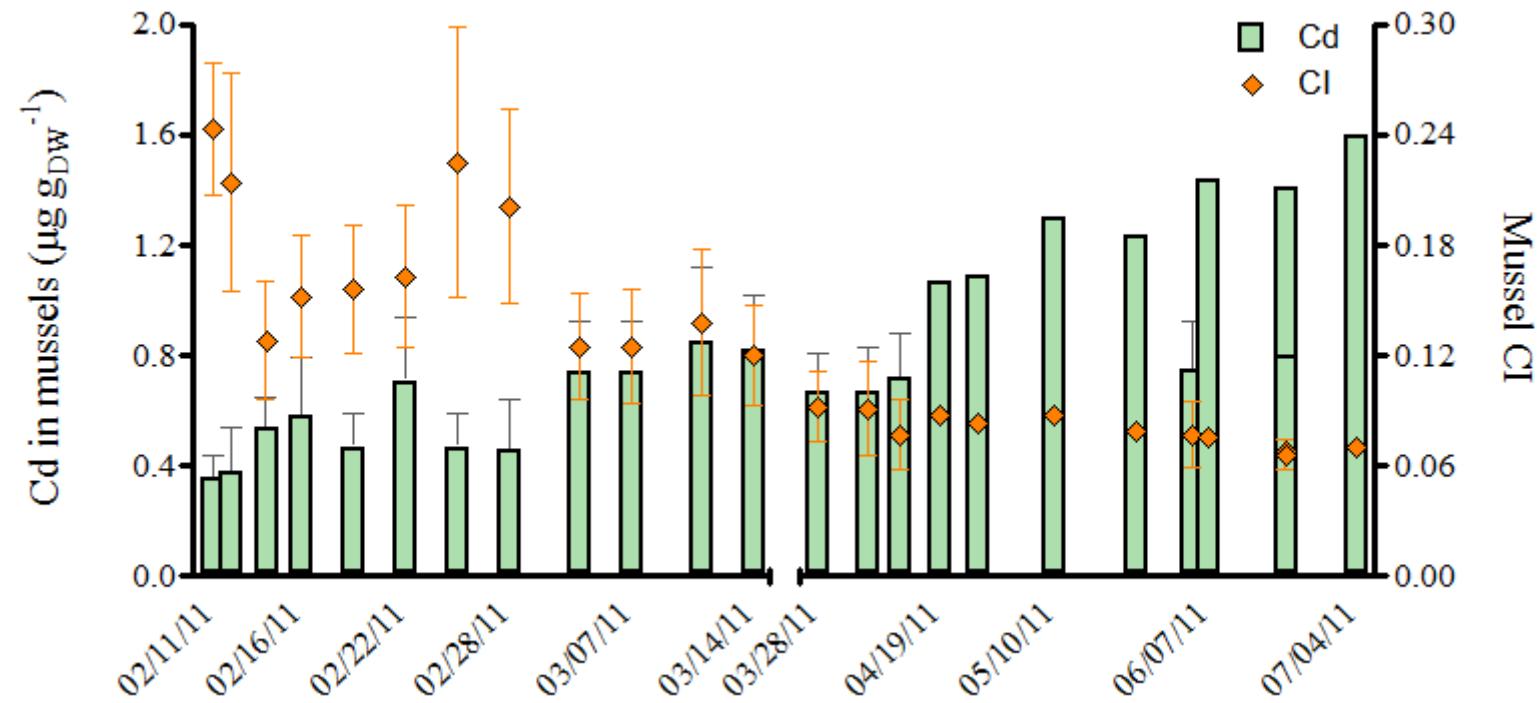




## TE kinetic in caged mussels

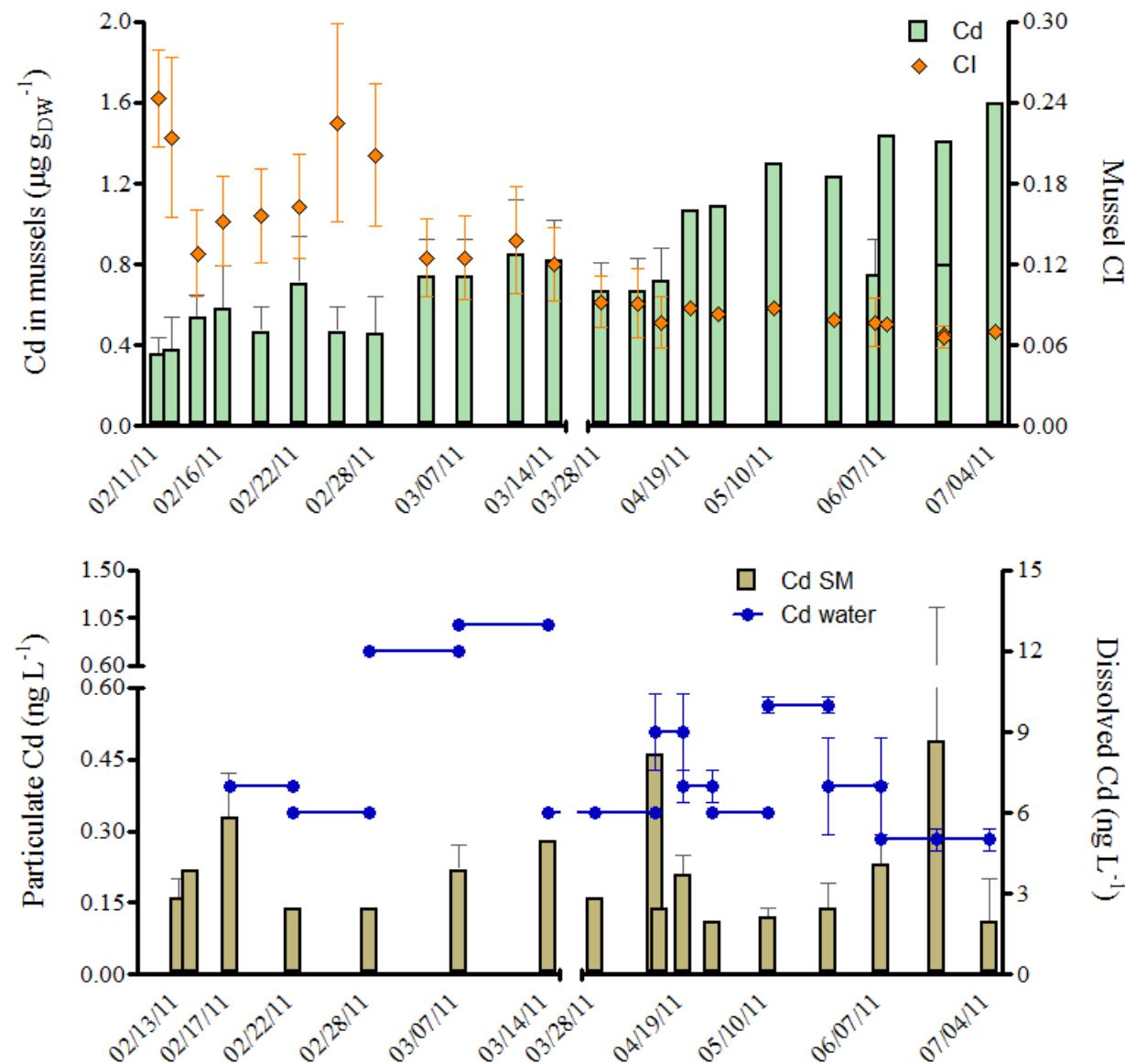
A  
P  
P  
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I  
C  
A  
T  
I  
O  
N

5





## TE kinetic in caged mussels

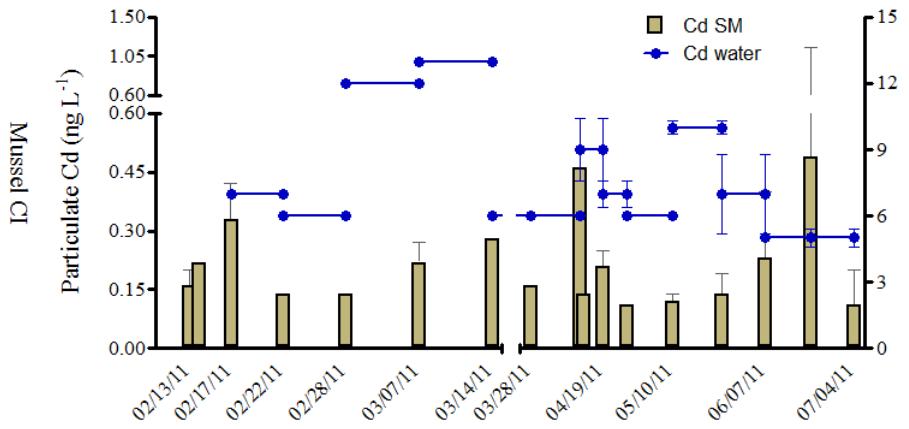
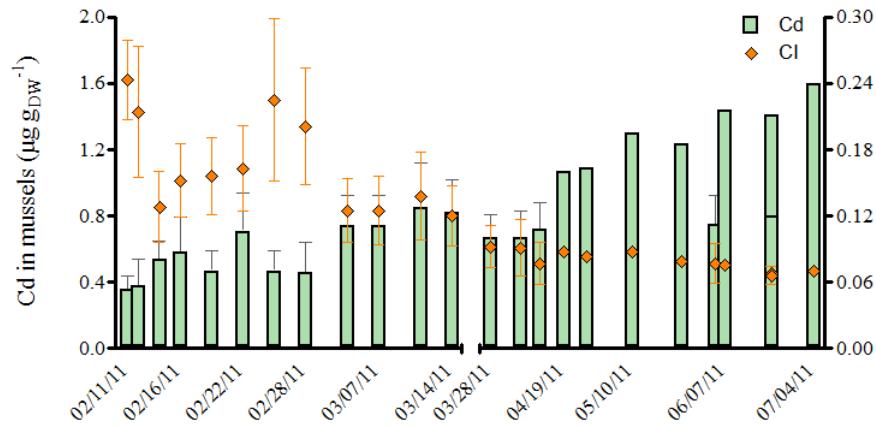
A  
P  
P  
L  
I  
C  
A  
T  
I  
O  
N



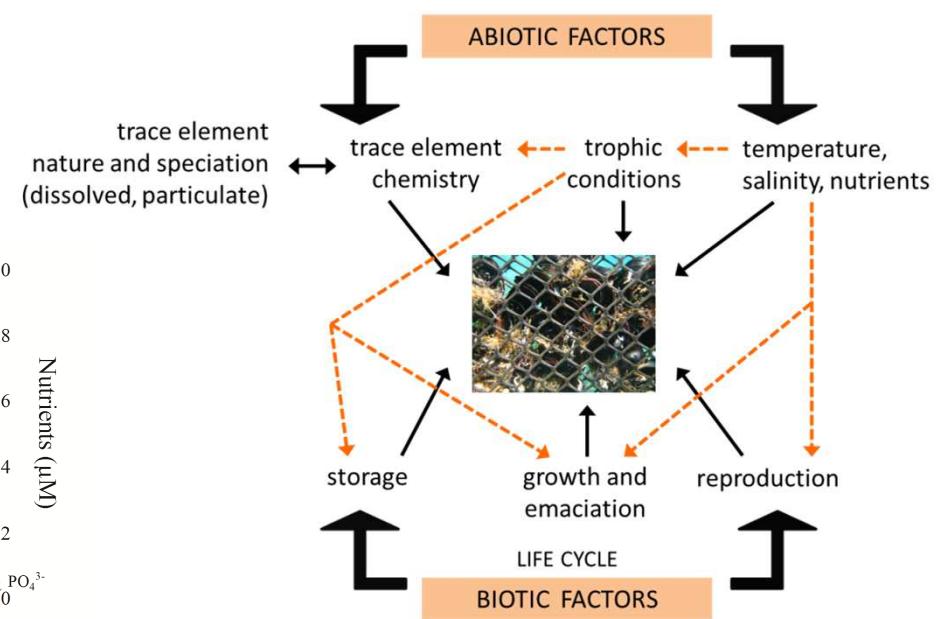
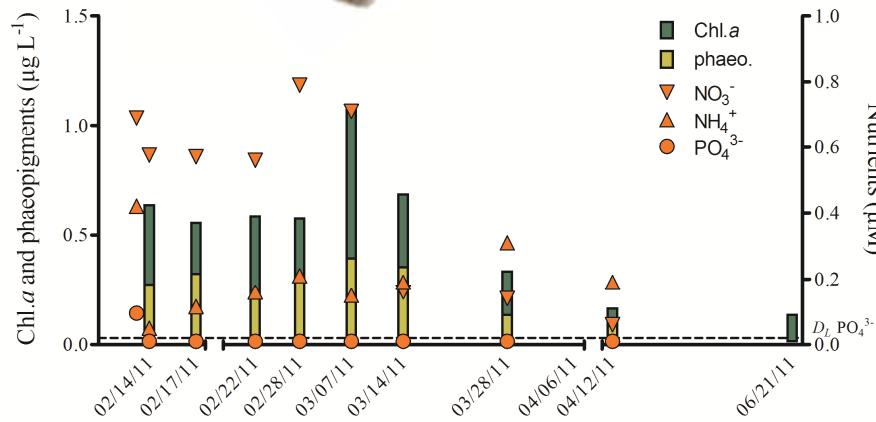
# TE kinetic in caged mussels

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what  
did you  
expect?



(modified after Casas, 2005)



## DGTs vs bioindicators

C  
O  
N  
C  
L  
U  
S  
I  
O  
N  
S

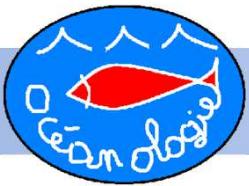
- Different and complementary information;
- Organism ecology in their chemical environment;
- Average TE concentrations over deployment time;
- Scheduled monitoring campaigns.



Combined use in ecological, ecotoxicological and ecosystemic approaches of marine coastal environment functioning.



**BIOMONITORING**  
SUBGROUPS  
METALLOID DIOXINS  
VALUES  
COMPLEX LEVEL  
TRIADIC ASSESSMENT  
INTERPRETATION DRIVING ENVIRONMENTAL  
GUIDANCE EXPOSURE POPULATION  
REASSESSMENT REPRESENTATIVE ACCURATELY  
BY BODY TOXIC EQUIVALENT TIME  
SCREENING PUBLIC  
ANALYTICAL CHEMISTRY  
RISKASSESSMENT  
QUENCHING CONCENTRATIONS  
ACADEMIC ROLES IDENTIFICATION  
DETERMINABLE MASC RECEIVED  
MINIMAD DETECTED CONFIRMED  
COLLABORATION ADMINISTRATORS BODY  
FOREWOODS REPORTING DATA  
DOSENSE PERSPECTIVE SAMPLING  
MONITORING PRESENCE SITETOPE  
PESCHICI PANEL LIPOPOLYSACCHARIDE  
BIPHENYLS CHLOROPHYLL  
BIFENYL BIENAL CHLOROPHYLL  
PESCHICI TETRAHALIDE  
(intheskies / Fotolia.com)



# Thank you for your attention

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Sebastián  
01-10-15

