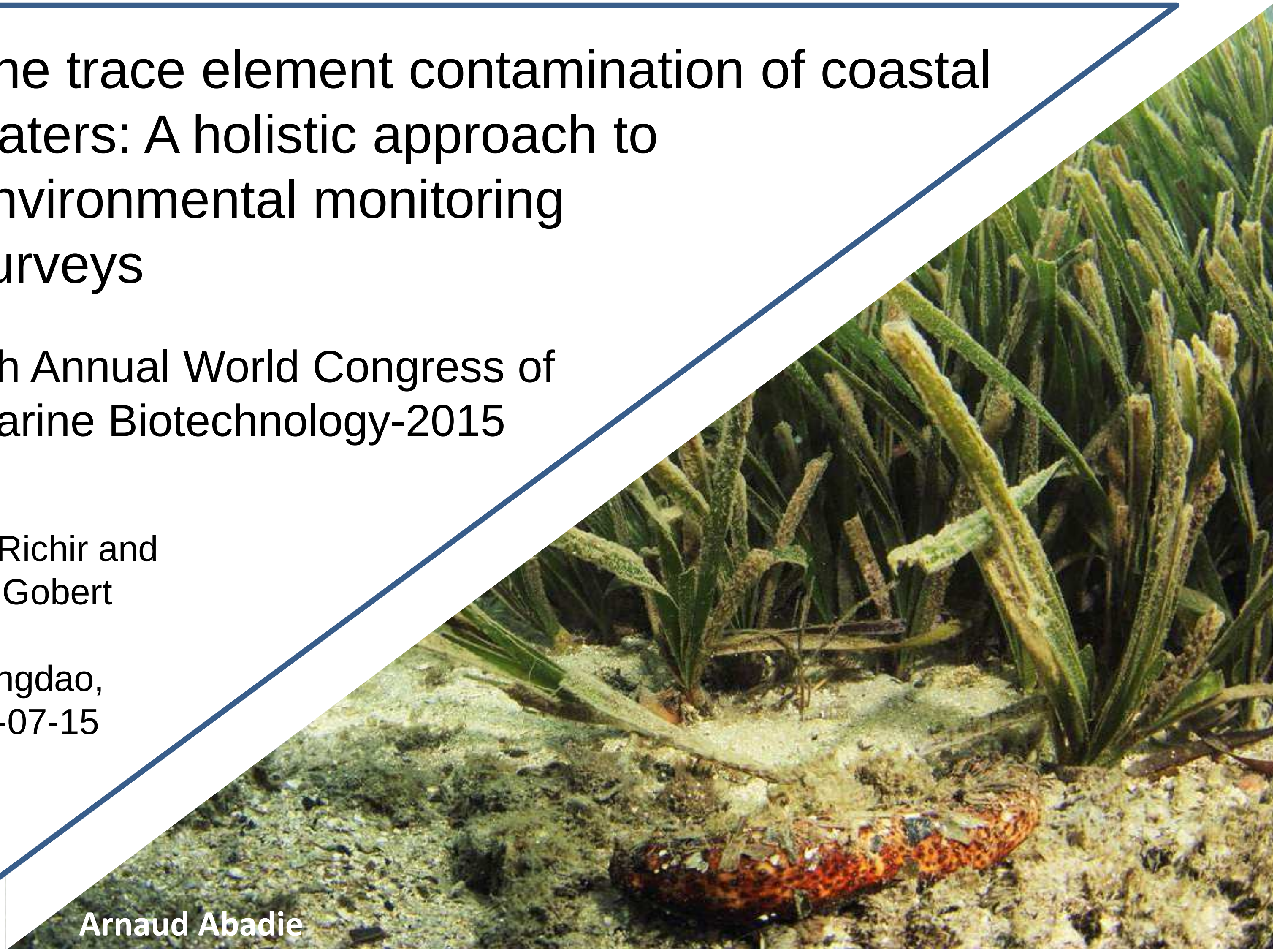
The trace element contamination of coastal waters: A holistic approach to environmental monitoring surveys

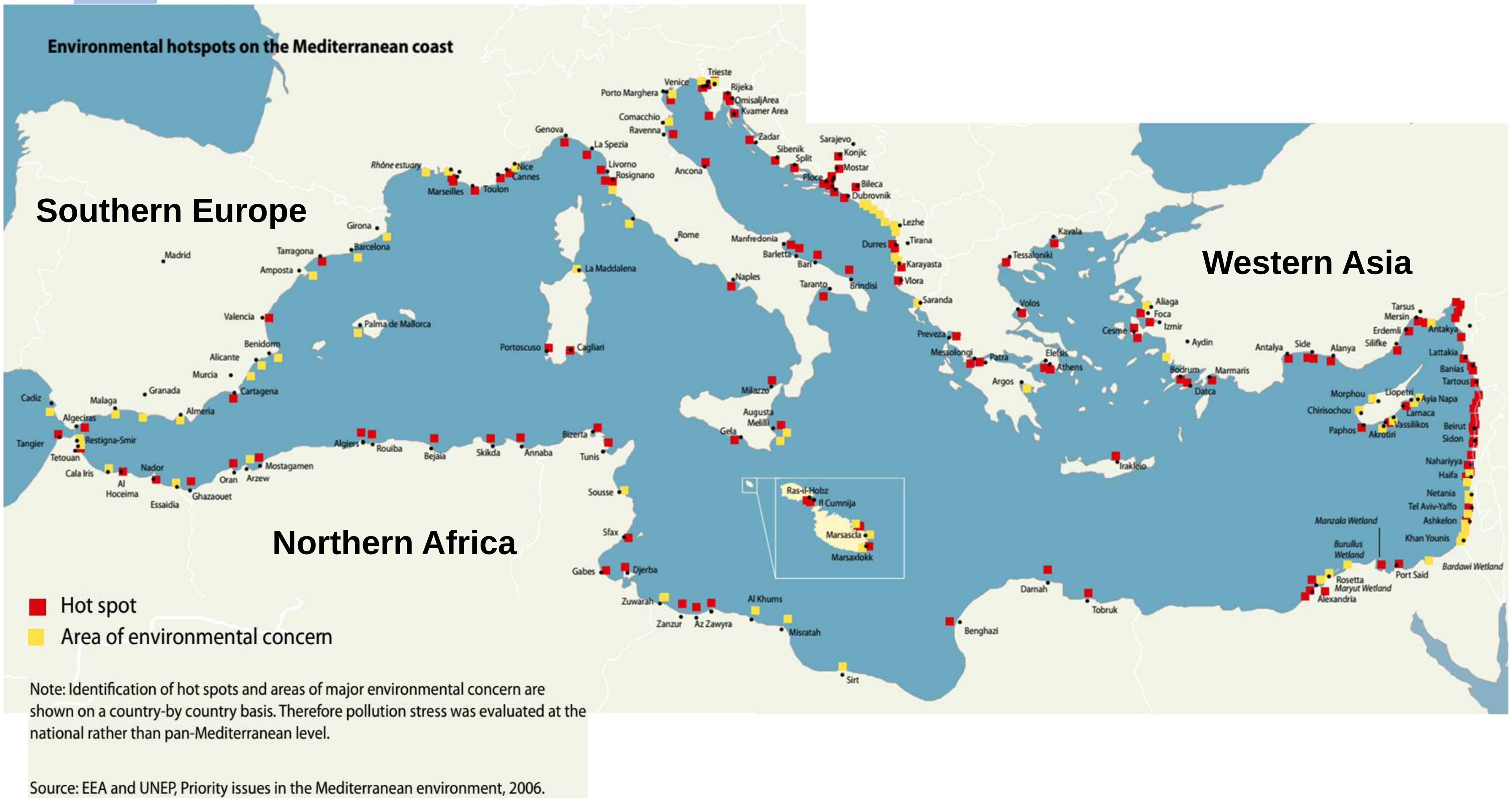
5th Annual World Congress of Marine Biotechnology-2015

J. Richir and
S. Gobert

Qingdao,
11-07-15



Coastal pollution of the Mediterranean



(UNEP/MAP, 2012; State of the Mediterranean Marine and Coastal Environment)

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PERIODIC TABLE of the ELEMENTS

DEPARTMENT OF SCIENCE AND TECHNOLOGY

ALKALI METALS
ALKALI EARTH METALS
TRANSITION METALS
OTHER METALS
OTHER NONMETALS
HALOGENS
NOBLE GASSES
RARE EARTH METALS

At room temperature the element is:

- Gas
- Liquid
- Natural solid
- Man-made solid [synthetic]

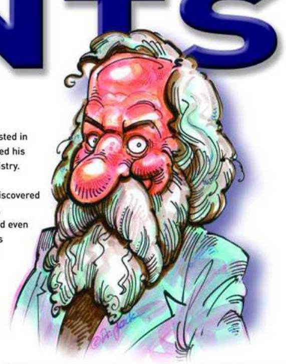
H — Symbol; Hydrogen — Element name; 1 — Atomic number; 1.01 — Atomic mass

DMITRI MENDELEYEV (1834 – 1907)

The Russian chemist, Dmitri Mendeleyev, 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 Mendeleyev'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. Mendeleyev 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 Mendeleyev.

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.



	IA 1	IIA 2	IIIB 3	IVB 4	VB 5	VIB 6	VIIB 7	VIII 8	VIII 9	VIII 10	IB 11	IIB 12	IIIA 13	IVA 14	VA 15	VIA 16	VIIA 17	VIIIA 18
1	H Hydrogen 1 1.01																	He Helium 2 4.00
2	Li lithium 3 6.94	Be Beryllium 4 9.01											B Boron 5 10.81	C Carbon 6 12.01	N Nitrogen 7 14.01	O Oxygen 8 16.00	F Fluorine 9 19.00	Ne Neon 10 20.18
3	Na Sodium 11 22.99	Mg Magnesium 12 24.31											Al Aluminium 13 26.98	Si Silicon 14 28.09	P Phosphorus 15 30.97	S Sulphur 16 32.06	Cl Chlorine 17 35.45	Ar Argon 18 39.95
4	K Potassium 19 39.10	Ca Calcium 20 40.08	Sc Scandium 21 44.96	Ti Titanium 22 47.88	V Vanadium 23 50.94	Cr Chromium 24 52.00	Mn Manganese 25 54.94	Fe Iron 26 55.85	Co Cobalt 27 58.93	Ni Nickel 28 58.69	Cu Copper 29 63.55	Zn Zinc 30 65.39	Ga Gallium 31 69.72	Ge Germanium 32 72.61	As Arsenic 33 74.92	Se Selenium 34 78.96	Br Bromine 35 79.90	Kr Krypton 36 83.80
5	Rb Rubidium 37 85.47	Sr Strontium 38 87.62	Y Yttrium 39 88.91	Zr Zirconium 40 91.22	Nb Niobium 41 92.91	Mo Molybdenum 42 95.94	Tc Technetium 43 (98)	Ru Ruthenium 44 101.07	Rh Rhodium 45 102.91	Pd Palladium 46 106.42	Ag Silver 47 107.87	Cd Cadmium 48 112.41	In Indium 49 114.82	Sn Tin 50 118.71	Sb Antimony 51 121.76	Te Tellurium 52 127.60	I Iodine 53 126.90	Xe Xenon 54 131.29
6	Cs Caesium 55 132.91	Ba Barium 56 137.33	Lanthanide Series	Hf Hafnium 72 178.49	Ta Tantalum 73 180.95	W Tungsten 74 183.85	Re Rhenium 75 186.21	Os Osmium 76 190.23	Ir Iridium 77 192.22	Pt Platinum 78 195.08	Au Gold 79 196.97	Hg Mercury 80 200.59	Tl Thallium 81 204.38	Pb Lead 82 207.20	Bi Bismuth 83 208.98	Po Polonium 84 (209)	At Astatine 85 (210)	Rn Radon 86 (222)
7	Fr Francium 87 (223)	Ra Radium 88 (226)	Actinide Series	Rf Rutherfordium 104 (261)	Db Dubnium 105 (262)	Sg Seaborgium 106 (263)	Bh Bohrium 107 (262)	Hs Hassium 108 (265)	Mt Meitnerium 109 (266)									

La Lanthanum 57 138.91	Ce Cerium 58 140.12	Pr Praseodymium 59 140.90	Nd Neodymium 60 144.24	Pm Promethium 61 (145)	Sm Samarium 62 150.36	Eu Europium 63 151.96	Gd Gadolinium 64 157.25	Tb Terbium 65 158.92	Dy Dysprosium 66 162.50	Ho Holmium 67 164.93	Er Erbium 68 167.26	Tm Thulium 69 168.93	Yb Ytterbium 70 173.04	Lu Lutetium 71 174.96
Ac Actinium 89 227.02	Th Thorium 90 232.03	Pa Protactinium 91 231.03	U Uranium 92 238.02	Np Neptunium 93 (237)	Pu Plutonium 94 (244)	Am Americium 95 (243)	Cm Curium 96 (247)	Bk Berkelium 97 (247)	Cf Californium 98 (251)	Es Einsteinium 99 (254)	Fm Fermium 100 (257)	Md Mendelevium 101 (258)	No Nobelium 102 (259)	Lr Lawrencium 103 (260)

FEST Foundation for Education, Science & Technology

Design and production: Loretta Steyn Graphic Design Studio - Pretoria **Illustrations:** Dr. Jack **Technical advisor:** Carl Ahlers - Experilab

POSIDONIA OCEANICA

Posidonia oceanica distribution

Geographical distribution of *Posidonia oceanica* (Michel, 2012; redrawn using data from Lipkin et al., 2003 ; Procaccini et al., 2003; Boudouresque et al., 2006; Gobert et al., 2006; Meinesz et al., 2009). 1: Gibraltar; 2: Almeria; 3: Oran; 4: Coasts of Syria, Israel and Lebanon; A: Rhone estuary; B: Po estuary; C: Nile estuary.

Objectives

OBJECTIVES

i. to assess, for the first time, the TE contamination in the entire Mediterranean biomonitored with *P. oceanica*;

ii. to propose a new 5-level water quality scale;

iii. to calculate coastal water pollution indices from bioaccumulated TE levels measured in that bioindicator;

iv. to produce, on the basis of these data, accurate maps of the contamination of the Mediterranean by TEs.

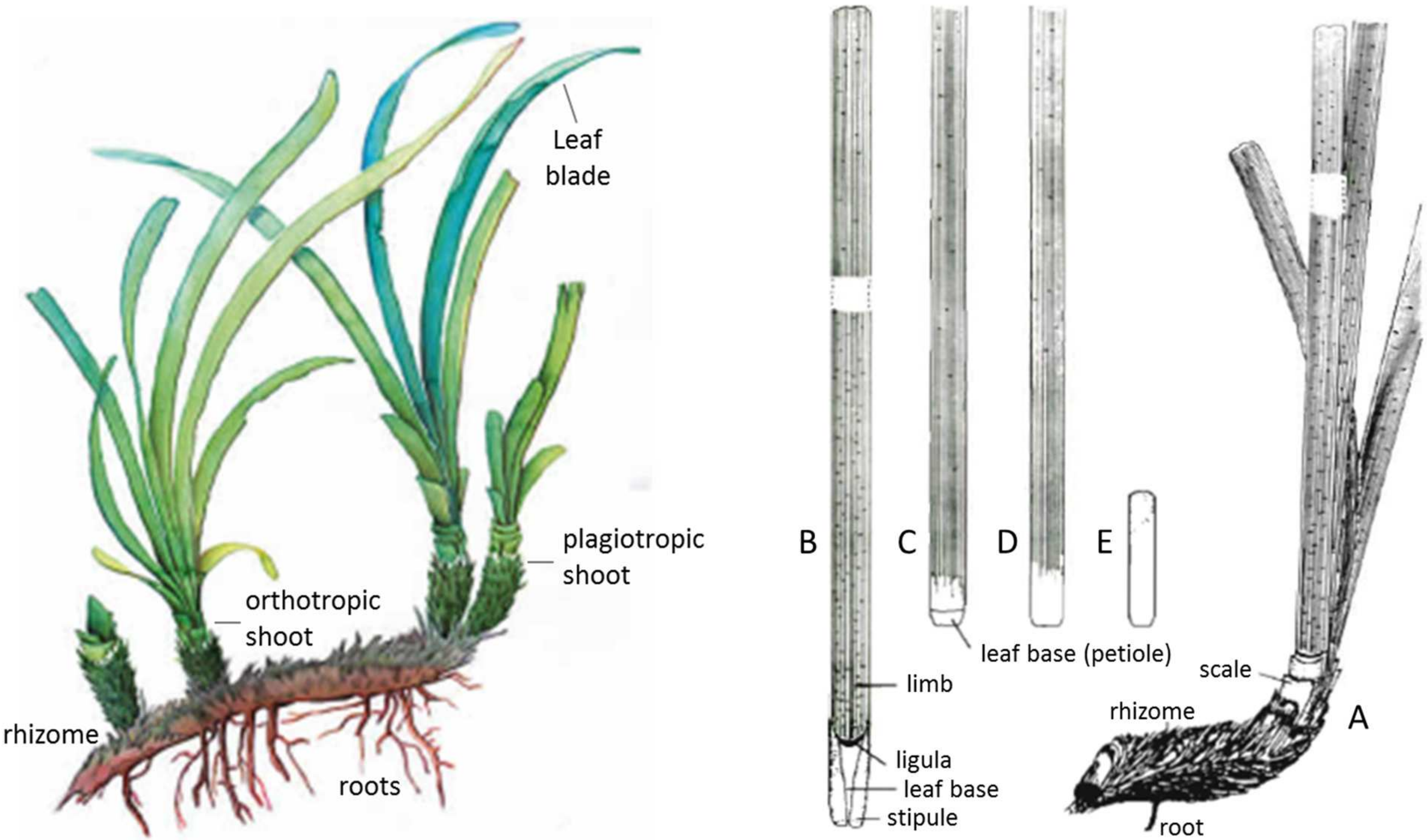
Overall aim of this work:

→ to develop a **holistic approach** in order to provide scientists, stakeholders and decision makers with **a global tool to bioassess the TE contamination severity** of Mediterranean coastal waters.

Sampling

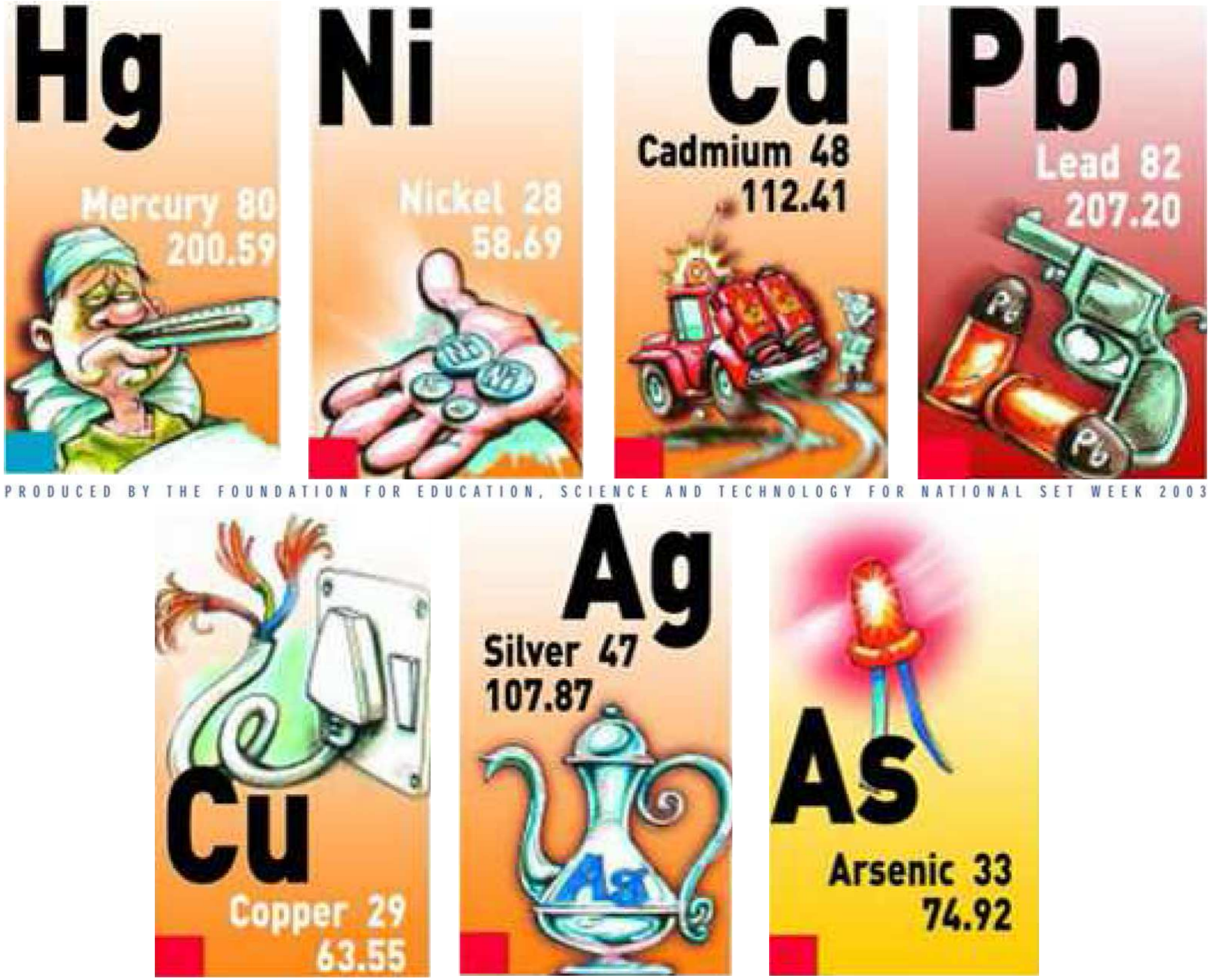
110 sites differing by their levels of exposure to contaminants sampled for *P. oceanica*.

P. oceanica compartmentalization



Left: *P. oceanica* shoots fixed on a plagiotropic rhizome. Right: (A) shoot of leaves on a plagiotropic rhizome; (B, C) adult leaves; (D) intermediate leaf; (E) juvenile leaf (modified after Libes and Boudouresque, 1987).

Trace elements monitored



M A T E R I A L

Maths and stats: monitoring

- Water quality scale
- Contamination indices:
  - Trace Element Spatial Variation Index (TESVI)
  - Trace Element Pollution Index (TEPI)

\-

Maths and stats: spatial analysis

M E T H O D S

- GIS mapping
- Principal component analysis
- Cluster analysis
- Correlation analysis

MATERIAL - METHODS

Maths and stats: 5-level water quality scale

qu. 1	qu. 2	qu. 3	qu. 4
0.6000	1.3333	1.7635	2.9333
0.6333	1.3333	1.7667	2.9667
0.6667	1.3667	1.7682	3.0012
0.7000	1.4000	1.8000	3.1253
0.7667	1.4000	1.8000	3.2113
0.8000	1.4000	1.8018	3.2333
0.8333	1.4333	1.8241	3.2333
0.8333	1.4333	1.8349	3.3667
0.8333	1.4333	1.8667	3.3667
0.8667	1.4511	1.9667	3.4705
0.9000	1.4667	1.9667	3.6000
1.0333	1.5000	2.0000	3.7667
1.0667	1.5000	2.0333	3.8000
1.0667	1.5180	2.1667	3.9000
1.1333	1.5667	2.2000	4.0667
1.1667	1.6000	2.2793	4.0667
1.1667	1.6000	2.3333	4.4333
1.1667	1.6333	2.3333	4.6000
1.2000	1.6333	2.3667	5.3333
1.2333	1.6333	2.4000	5.4790
1.2333	1.6667	2.4333	5.5667
1.2667	1.6667	2.5333	5.9129
1.2667	1.7000	2.6333	5.9250
1.2667	1.7000	2.6667	6.0751
1.2667	1.7000	2.7333	6.1230
1.2667	1.7333	2.9333	7.9000
1.3000	1.7333	2.9333	8.5667
1.3000			14.5000

Quartile means

Superior limit of quartiles

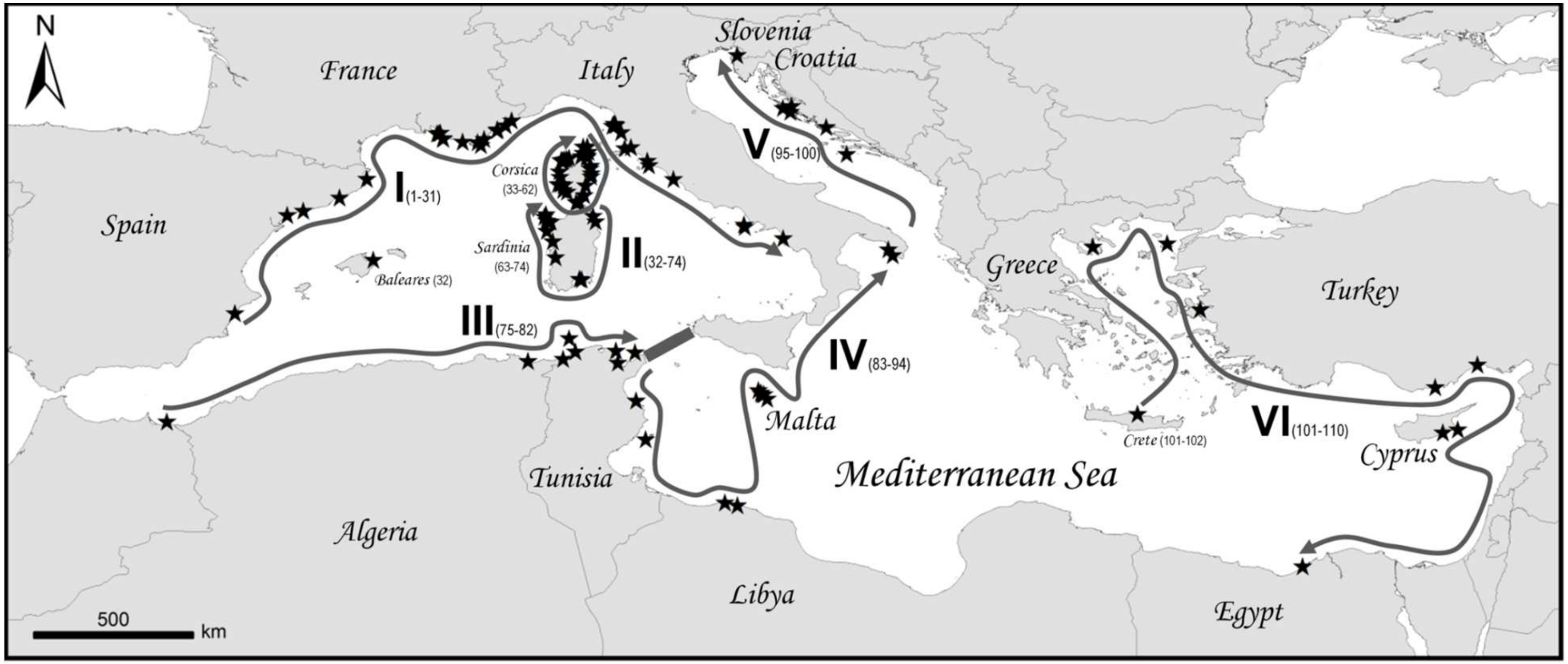
	Pb
quartile 1	1.3083
quartile 2	1.7484
quartile 3	2.9333
quartile 4	14.5000

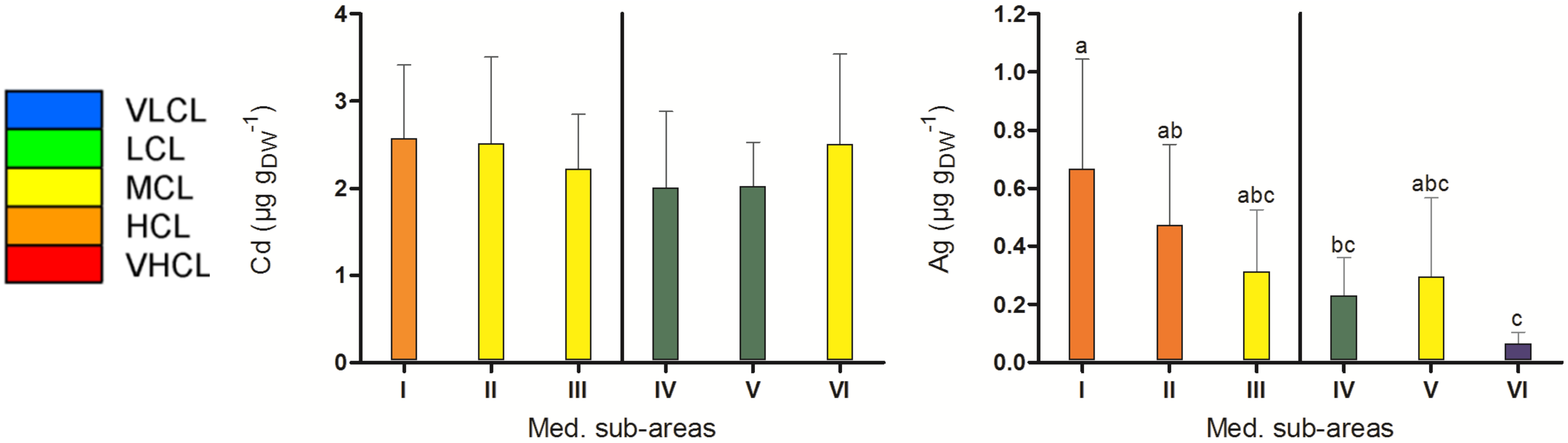
5 contamination levels

- < 1st qu. mean : very low CL
- 1st-2nd qu. mean: low CL
- 2nd-3rd qu. mean: medium CL
- 3rd-4th qu. mean: high CL
- > 4th qu. mean: very high CL

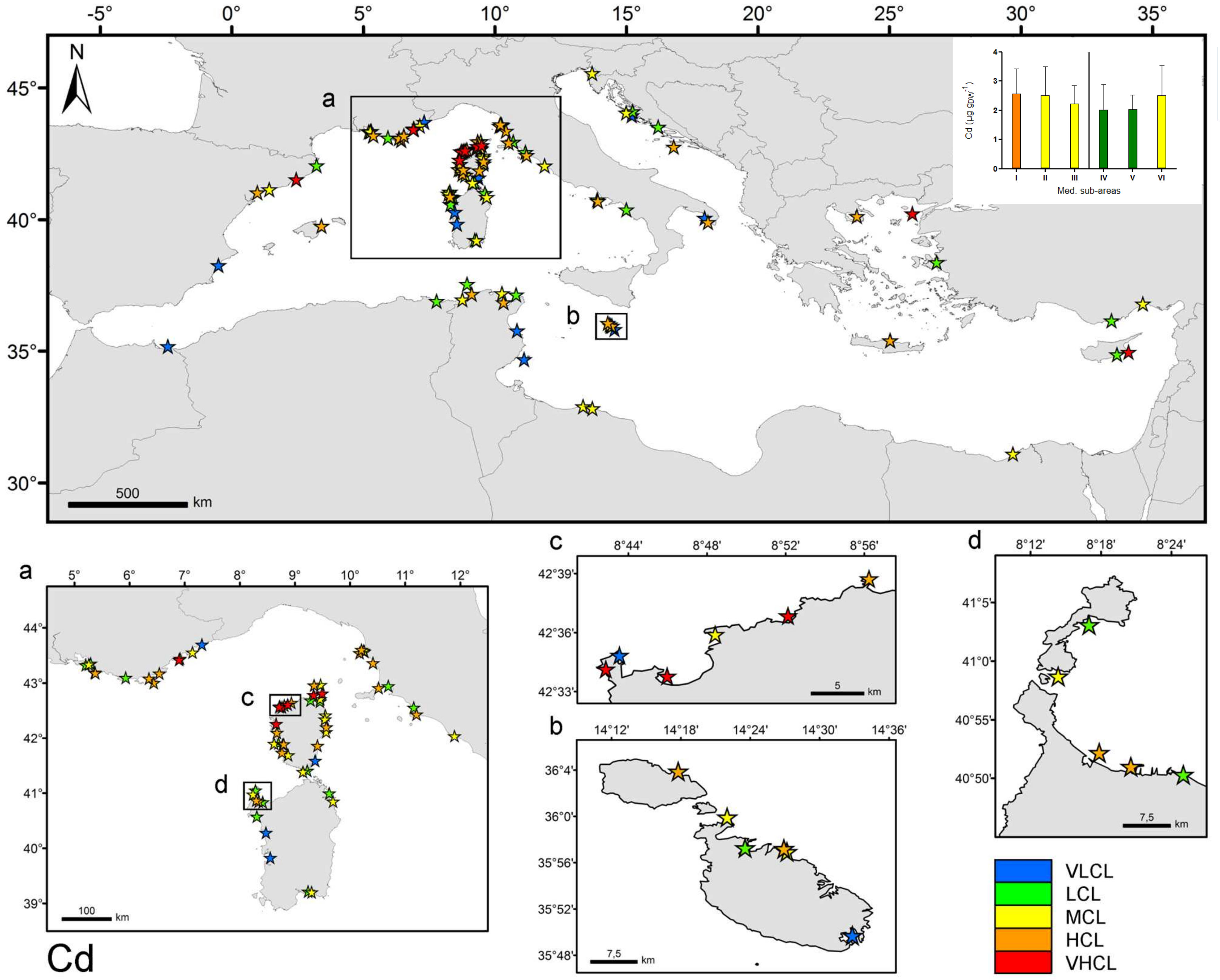
RESULTS - DISCUSSION

Sub-areas differences

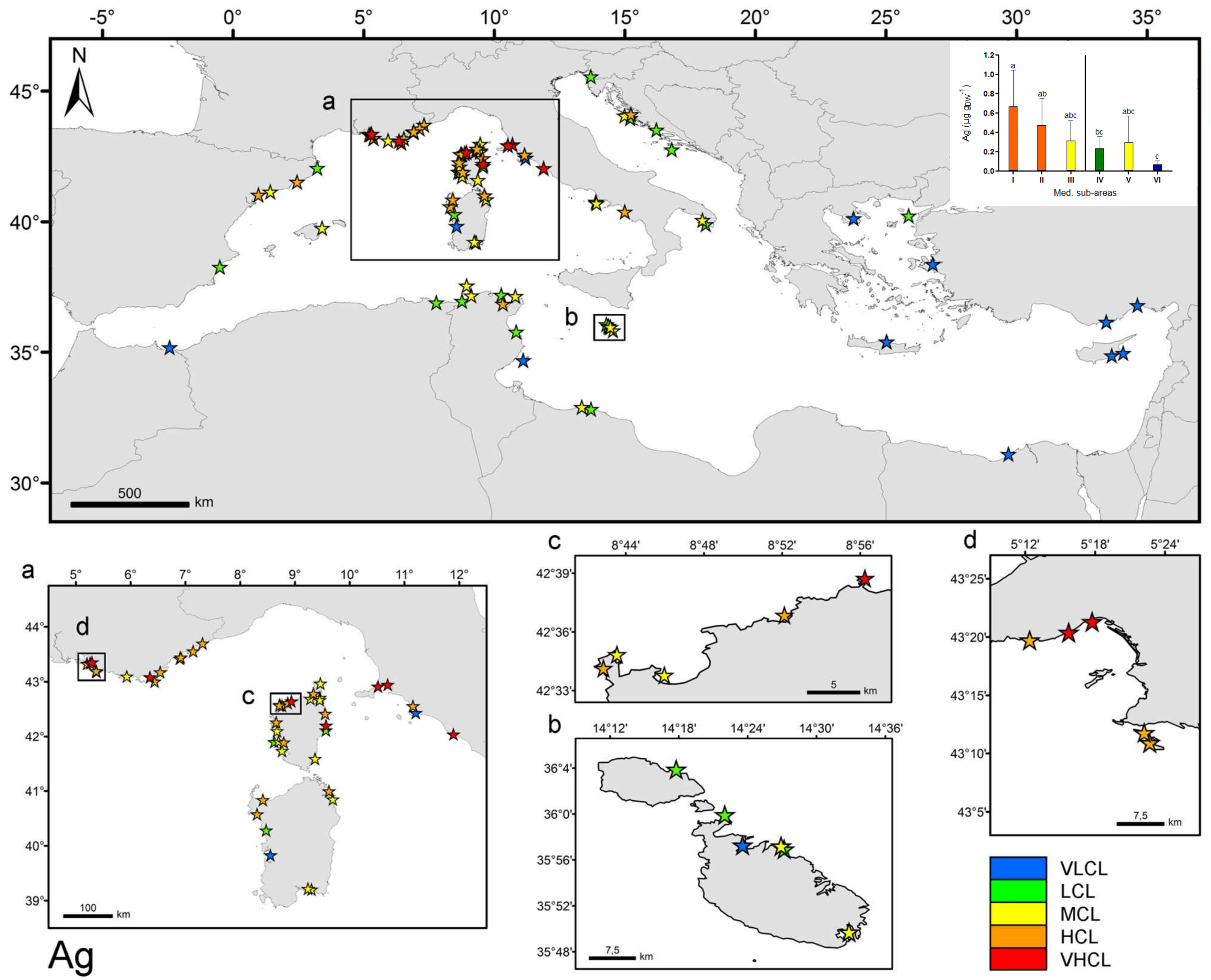




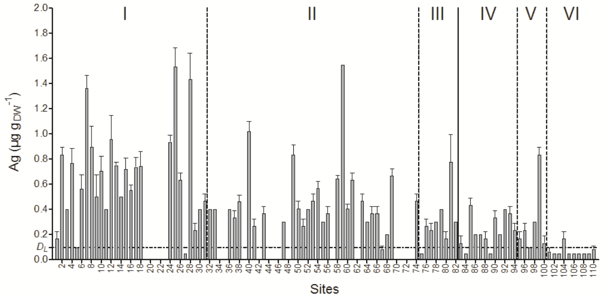
RESULTS - DISCUSSION

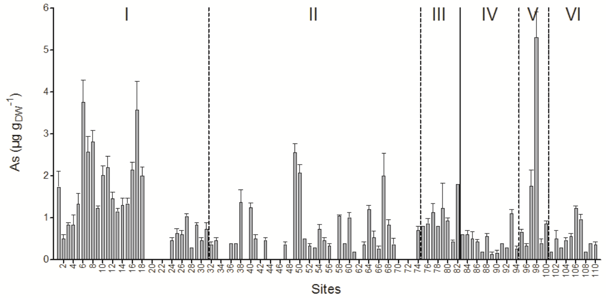


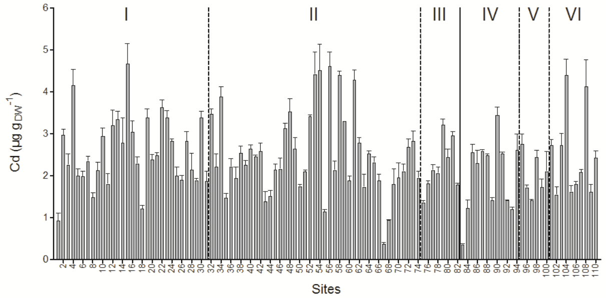
R E S U L T S - D I S C U S S I O N

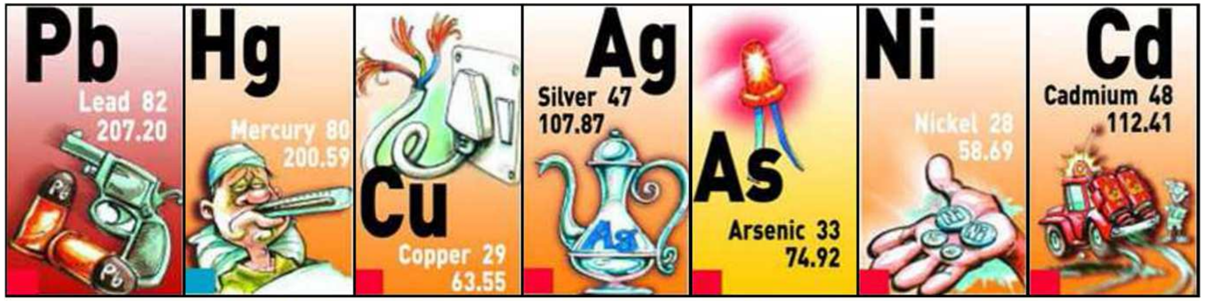


Maths and stats: pollution indices









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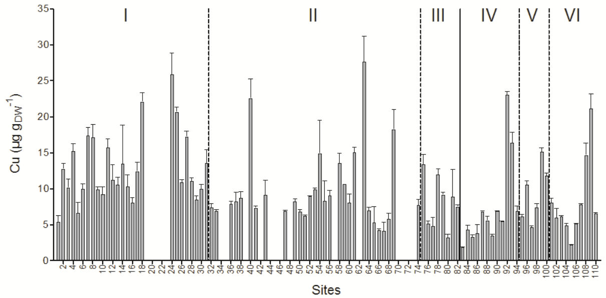
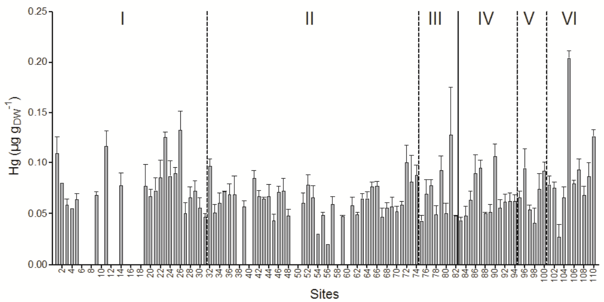
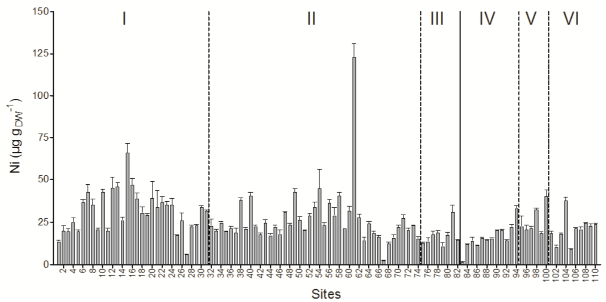
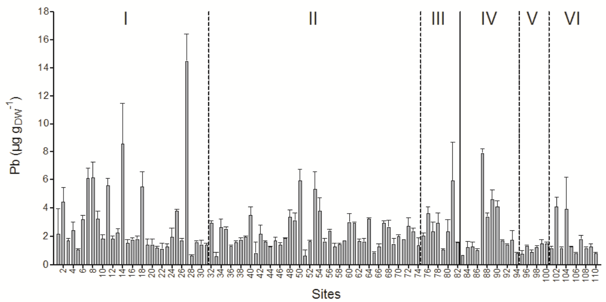
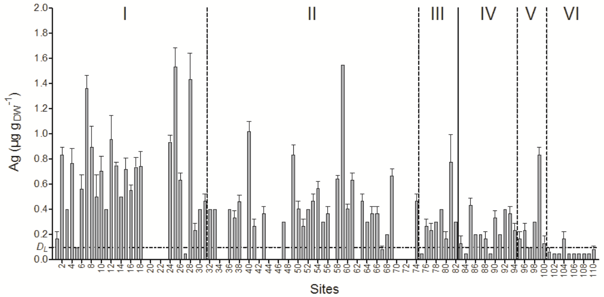


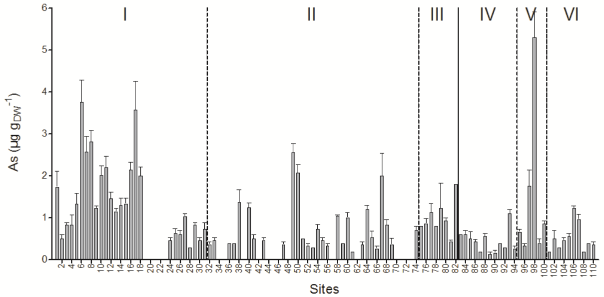


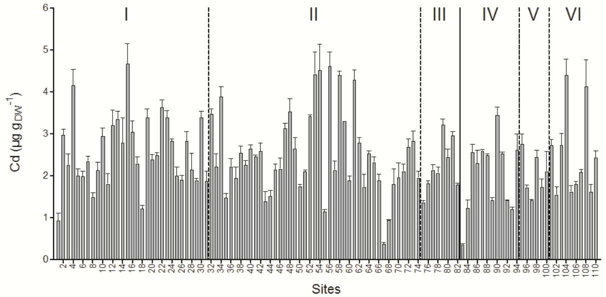




Maths and stats: pollution indices

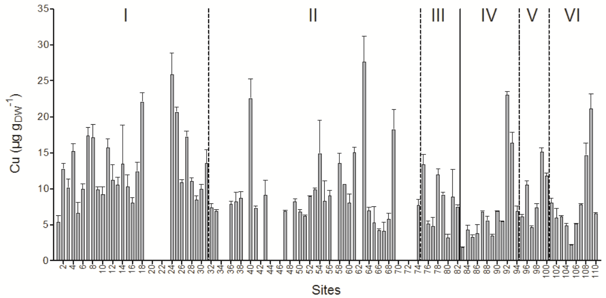


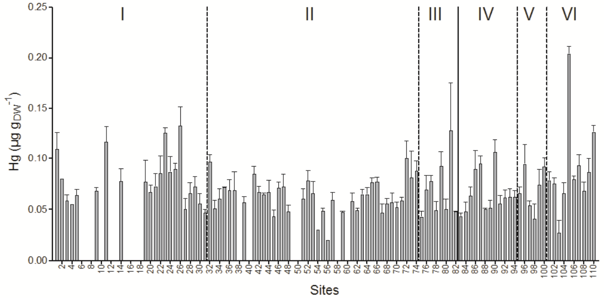


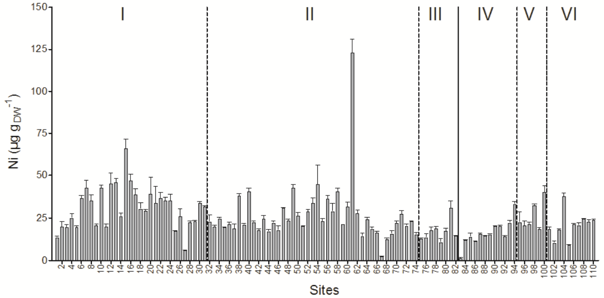


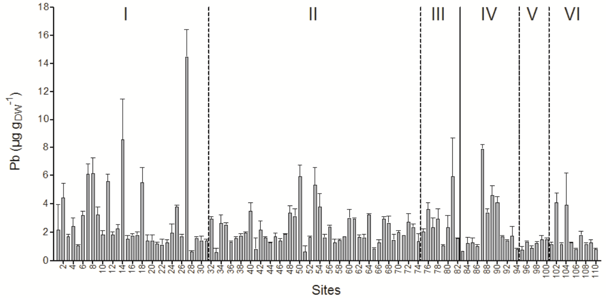
- ❖ How to order and to compare TEs according to the overall spatial variability of their environmental levels through the whole of a studied area ?

- ❖ How to compare global pollution levels in TEs between several monitored sites ?



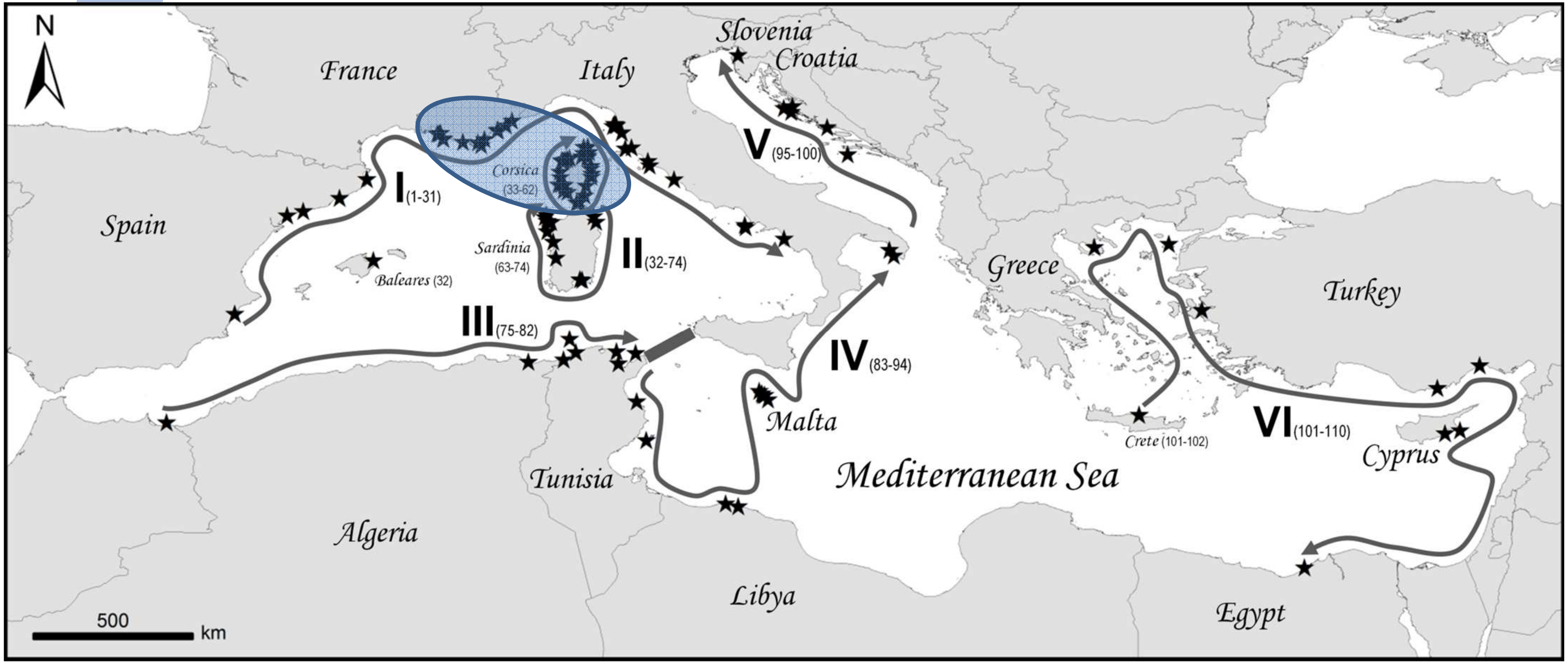






Sampling

Pollution indices developed first for the French Mediterranean littoral.



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ELSEVIER

A reassessment of the use of *Posidonia oceanica* and *Mytilus galloprovincialis* to biomonitor the coastal pollution of trace elements: New tools and tips

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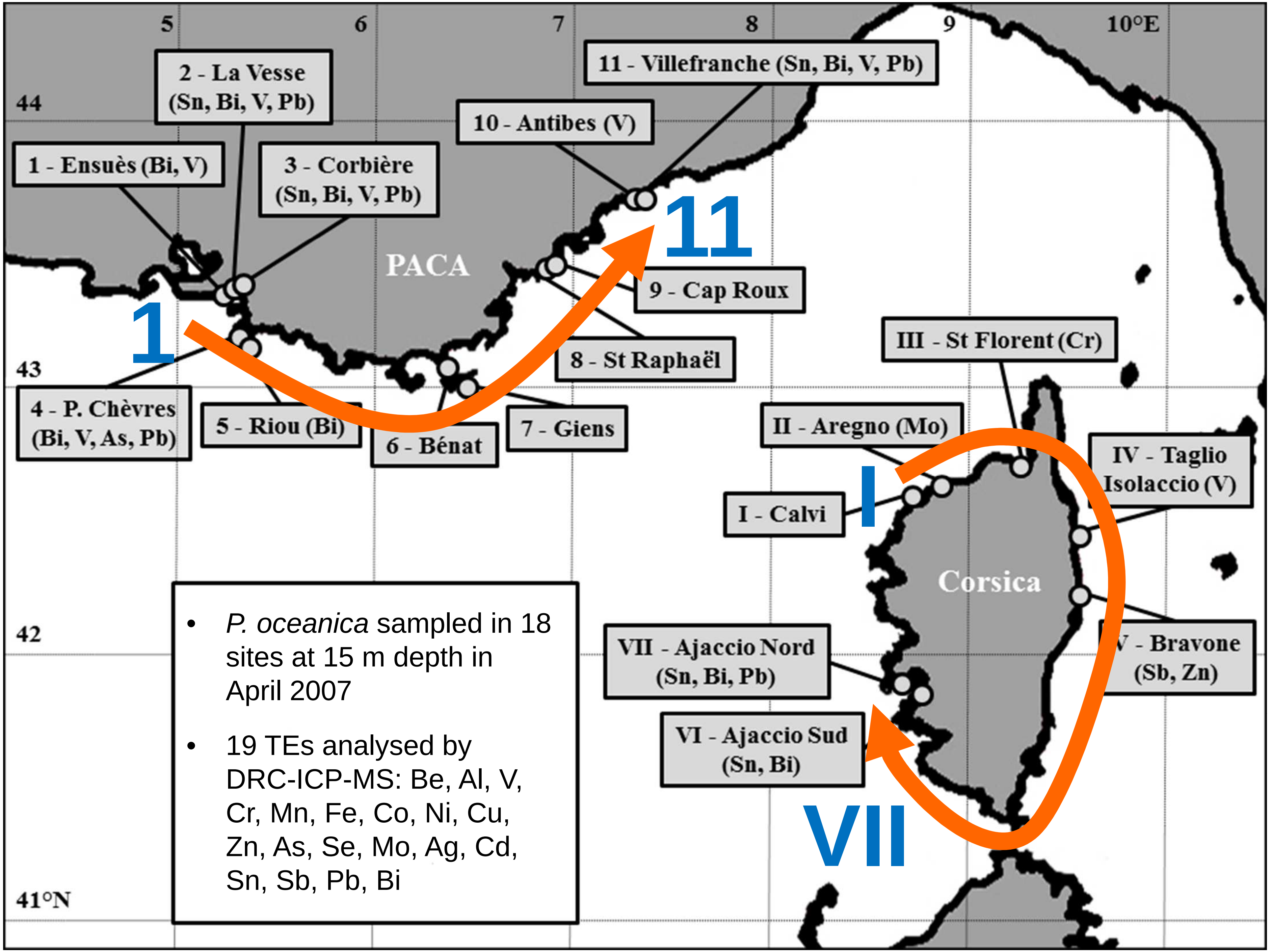


- *P. oceanica* sampled in 18 sites at 15 m depth in April 2007
- 19 TEs analysed by DRC-ICP-MS: Be, Al, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Mo, Ag, Cd, Sn, Sb, Pb, Bi

Trace Element Spatial Variation Index

M A T E R I A L - M E T H O D S

❖ How to order and to compare TEs according to the overall spatial variability of their environmental levels through the whole of a studied area ?

Trace Element Spatial Variation Index (TESVI)

$$TESVI = [(x_{max}/x_{min}) / (\sum(x_{max}/x_i)/n)] * SD$$

where:

- x_{max} and x_{min} are the maximum and minimum mean concentrations recorded among the n sites,
- x_i are mean concentrations recorded in each of the n sites,
- SD is the standard deviation of the weighted sum $\sum(x_{max}/x_i)/n$.

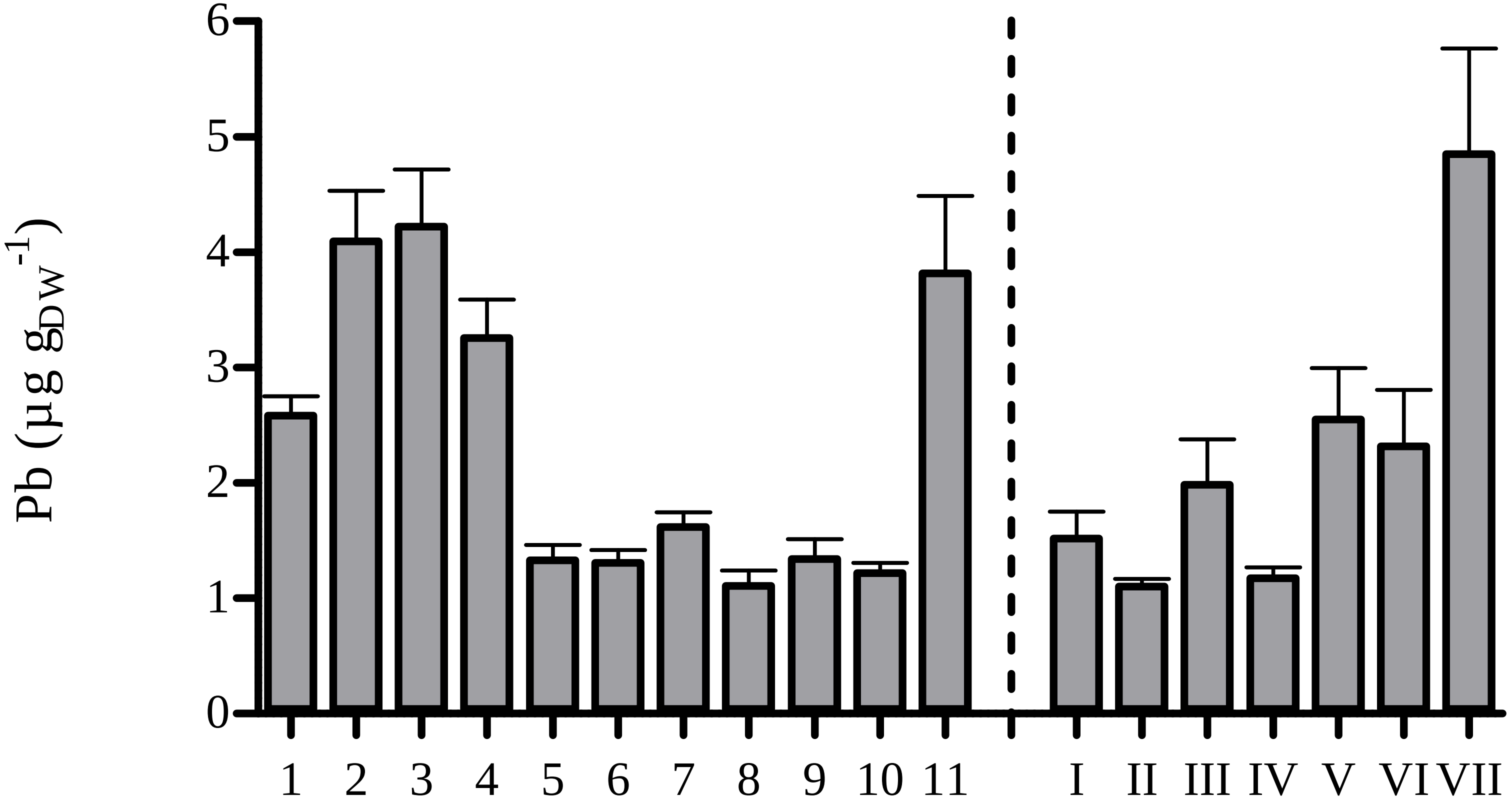
➡ The highest the index value, the more environmental levels of a TE globally vary (punctual contaminations and overall coastal spatial heterogeneity of TE levels taken into account) through the whole of the studied area the index is applied to.

TESVI value calculation

T
E
S
V
I

Trace Element Spatial Variation Index (TESVI)

$$TESVI = [(x_{max}/x_{min}) / (\sum(x_{max}/x_i)/n)] * SD$$



TESVI value calculation

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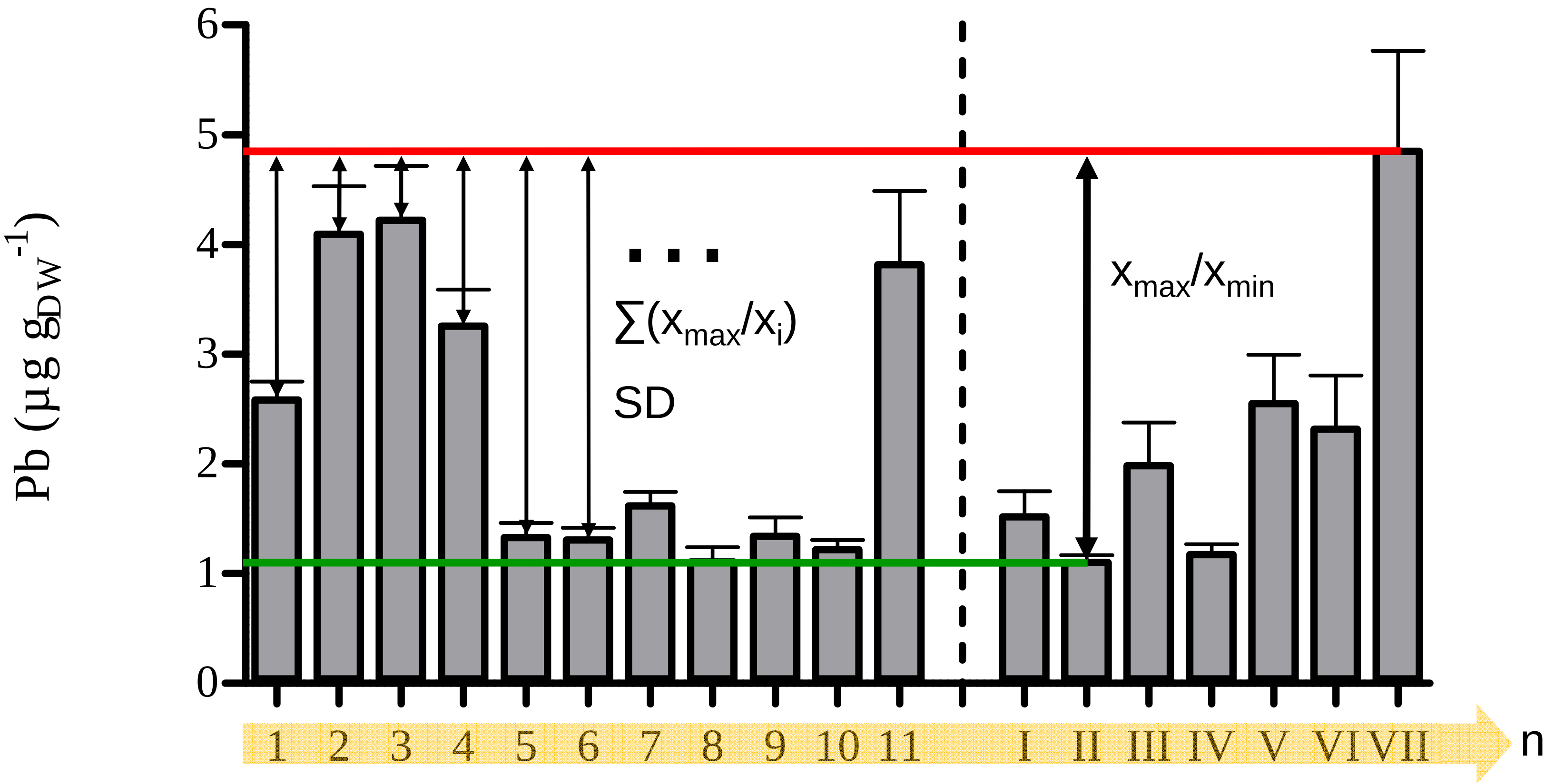
Trace Element Spatial Variation Index (TESVI)

$$TESVI = [(x_{max}/x_{min}) / (\sum(x_{max}/x_i)/n)] * SD$$



TESVI graphical representation

T
E
S
V
I

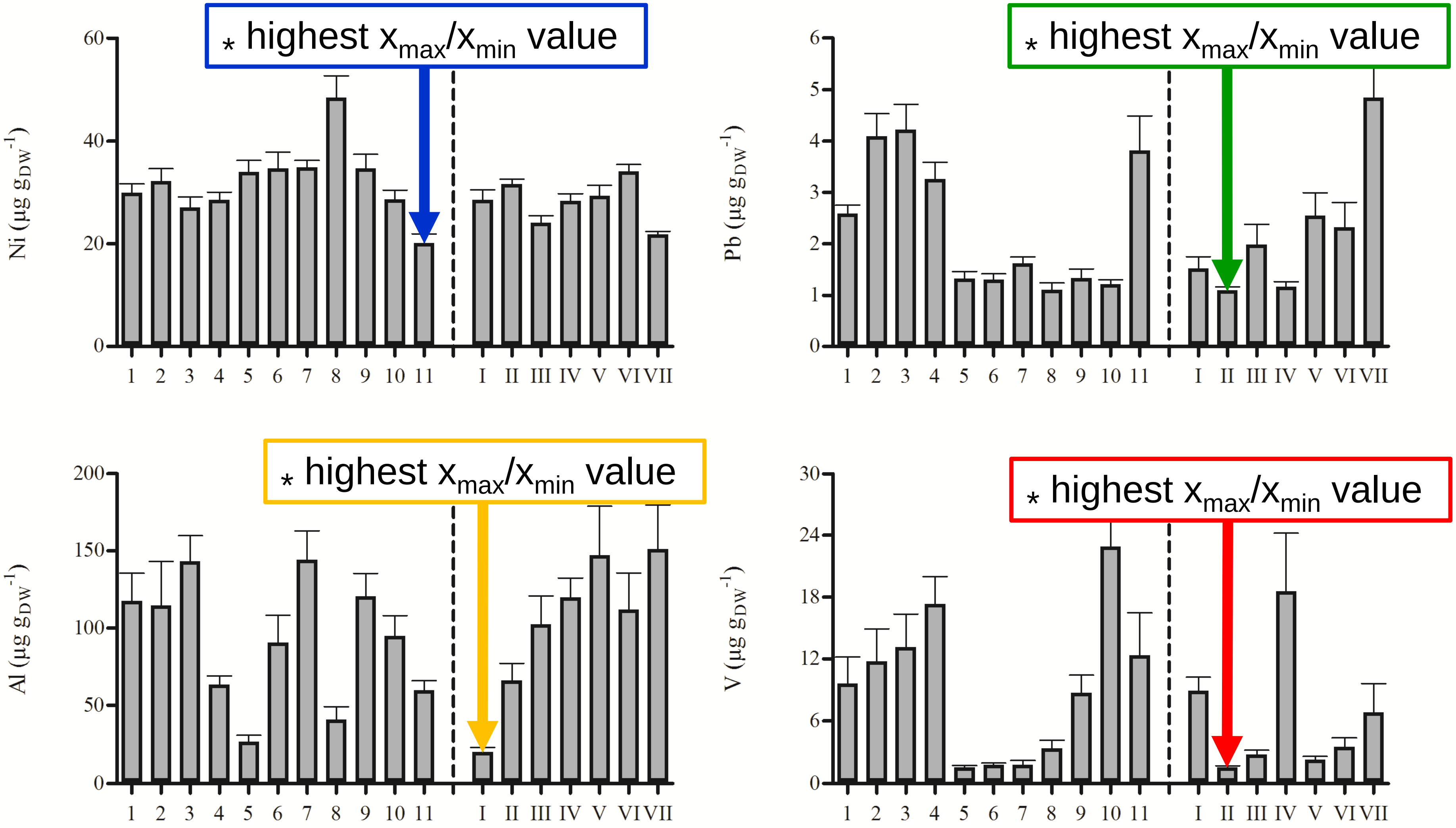
A. TEs broadly monitored with *P. oceanica*

	x_{max}/x_{min}	$\sum(x_{max}/x_i)/18 \pm SD$	TESVI	Site x_{max}
Cr	6.0	3.6 ± 1.3	2.2	St Florent
Fe	4.4	2.0 ± 0.9	1.9	Bravone
Ni	2.4	1.6 ± 0.3	0.5	St Raphaël
Cu	3.4	1.9 ± 0.7	1.2	Villefranche
Zn	19.6	13.3 ± 4.4	6.5	Bravone
Cd	3.9	1.9 ± 0.7	1.4	St Raphaël
Pb	4.4	2.7 ± 1.2	2.0	Ajaccio N.
Be	3.1	1.6 ± 0.6	1.0	Ajaccio N.
Al	7.5	2.2 ± 1.8	6.1	Ajaccio N.
V	14.5	5.9 ± 5.0	12.3	Antibes
Mn	2.2	1.6 ± 0.4	0.5	St Raphaël
Co	2.9	1.8 ± 0.5	0.7	St Raphaël
As	10.6		4.9	P. des Chèvres
Se	1.7		0.3	Calvi
Mo	22.8		10.5	Aregno
Ag	3.1		0.9	La Vesse
Sn (BAL)	6.9		3.8	Corbière
Sb	4.4	3.6 ± 0.7	0.9	Bravone
Bi	13.6	6.1 ± 3.5	7.9	P. des Chèvres

TESVI values were listed in ascending order :

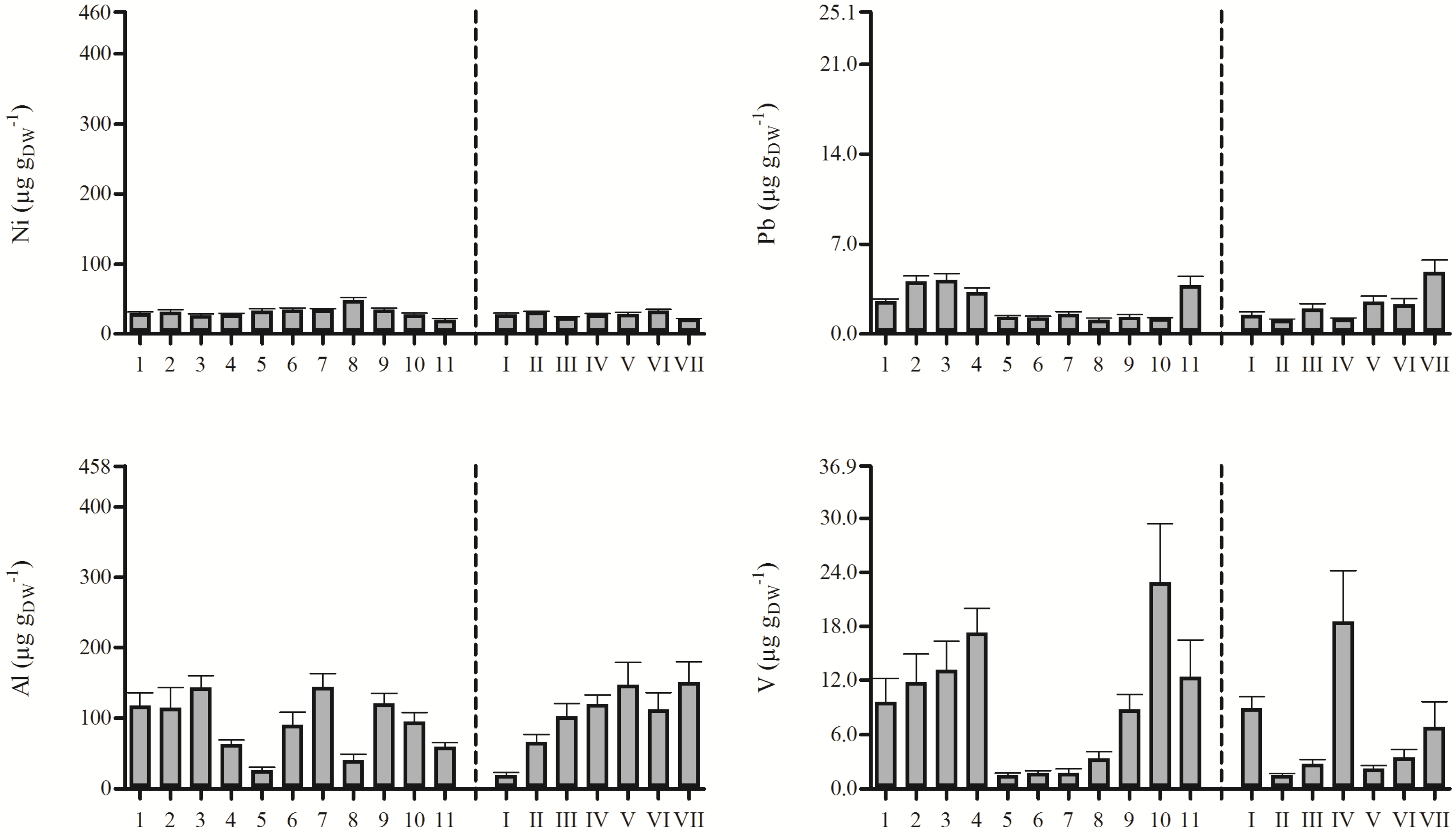
Se, Ni, Mn, Co, Sb, Ag, Be, Cu, Cd, Fe, Pb, Cr, Sn, As, Al, Zn, Bi, Mo, V

TESVI graphical representation



TESVI values were listed in ascending order :
Se, **Ni**, Mn, Co, Sb, Ag, Be, Cu, Cd, Fe, **Pb**, Cr, Sn, As, **Al**, Zn, Bi, Mo, **V**

TESVI graphical representation

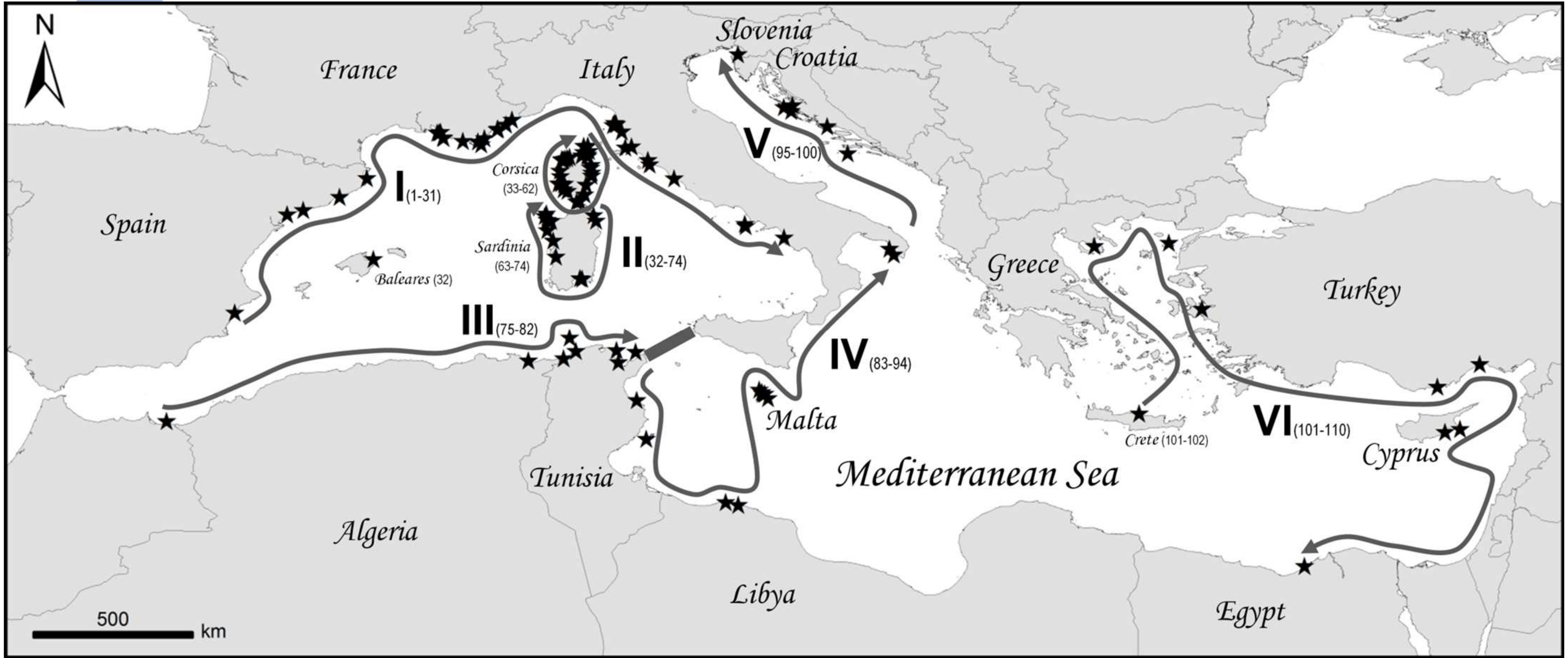


TESVI values were listed in ascending order :

Se, **Ni**, Mn, Co, Sb, Ag, Be, Cu, Cd, Fe, **Pb**, Cr, Sn, As, **Al**, Zn, Bi, Mo, **V**

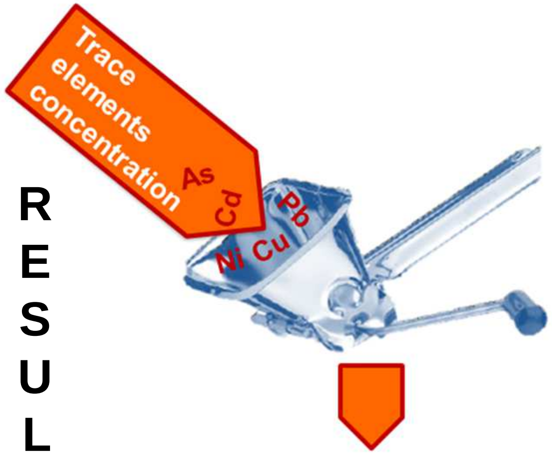
Sampling

110 sites differing by their levels of exposure to contaminants sampled for *P. oceanica*.



Spatial variability

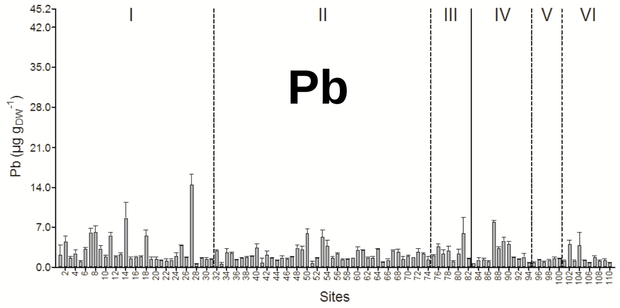
R E S U L T S - D I S C U S S I O N

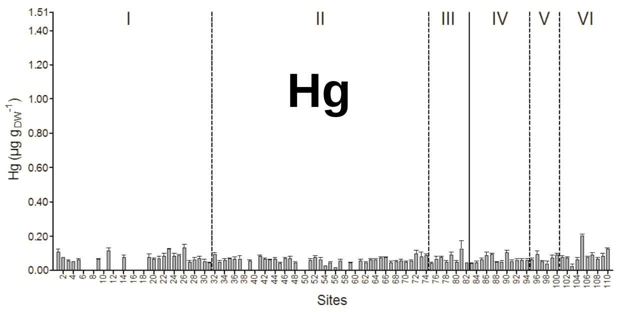


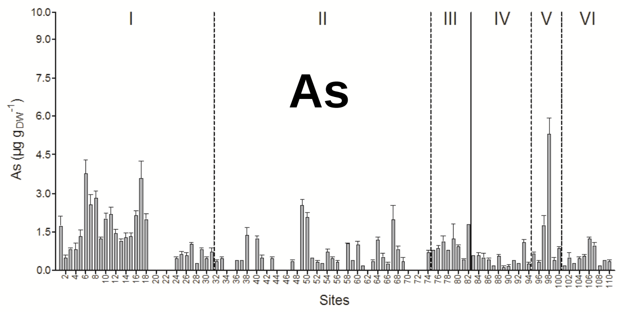
Index values

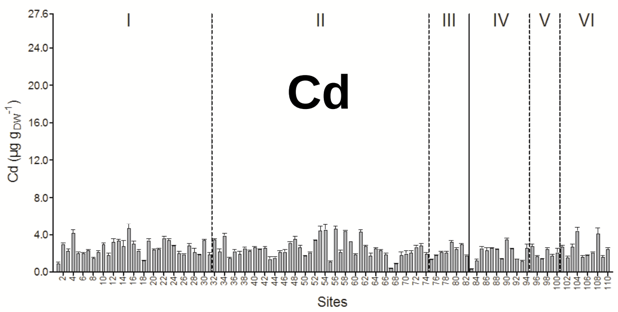
TE	TESVI
Hg	3.9
Cd	8.7
Cu	9.2
Pb	13.3
As	29.4
Ag	34.9
Ni	92.7

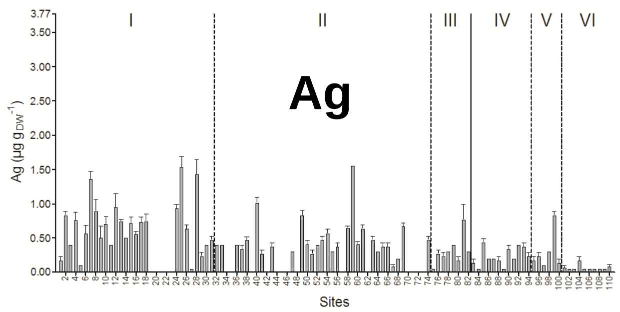
Proportional ordinate **scaling** between TEs:

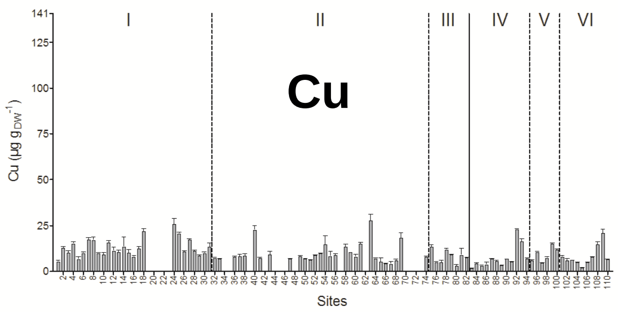


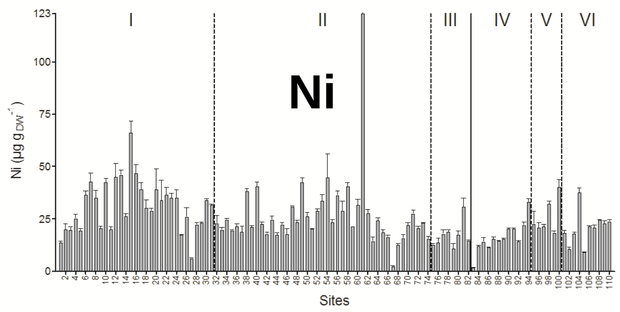












Trace Element Pollution Index

How to compare global pollution levels in TEs between several monitored sites ?

Trace Element Pollution Index (TEPI)

$$TEPI = (Cf_1 * Cf_2 \ldots Cf_n)^{1/n},$$

a weighted version of the Metal Pollution Index (MPI) of Usero et al. (1996, MPB)

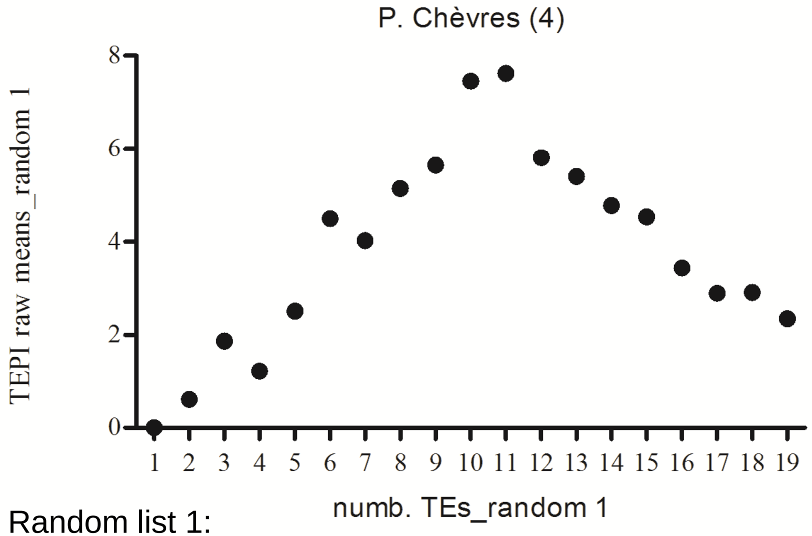
where:

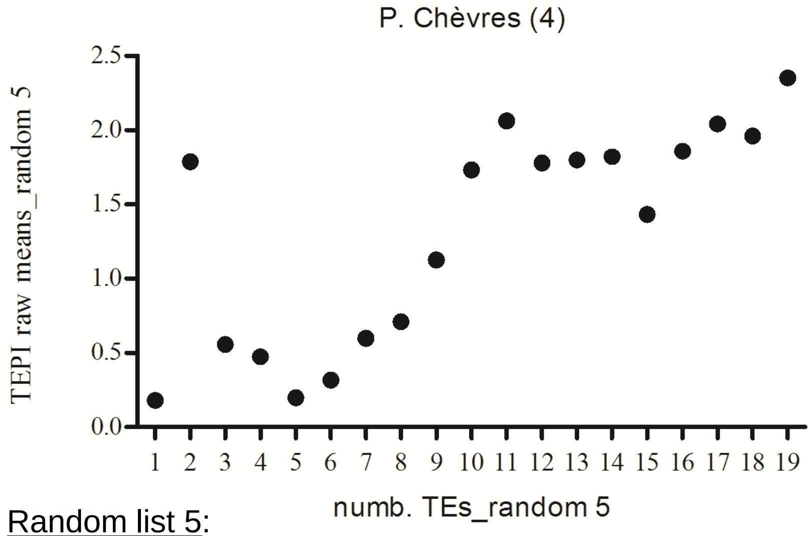
- Cf_n is the mean normalized concentration of the TE n in a given monitored site.

The highest the index value, the more the monitored site is globally contaminated in TEs compared to the others.

T
E
P
I

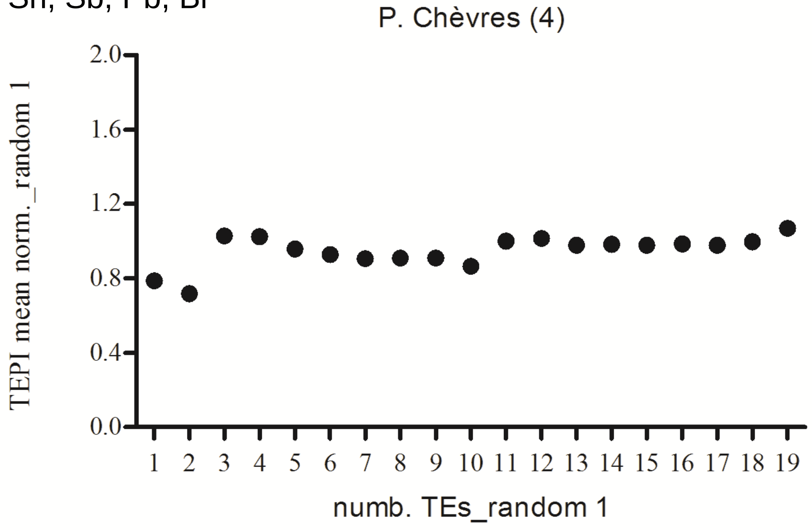
Mean normalization

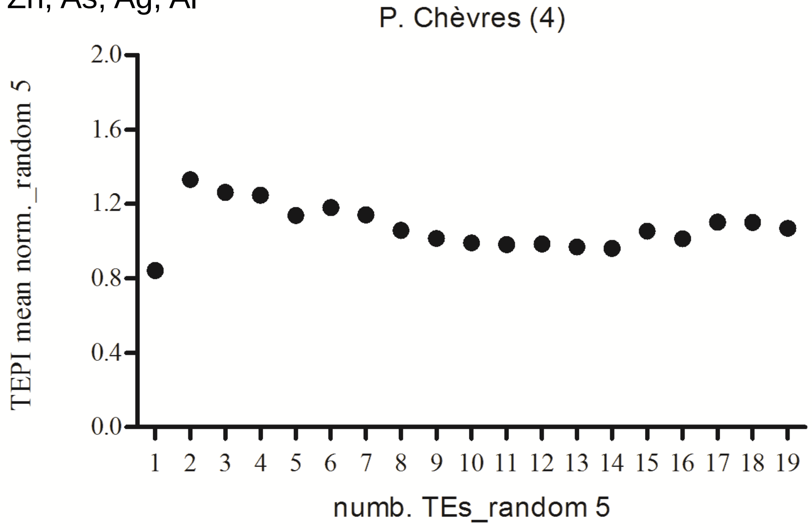




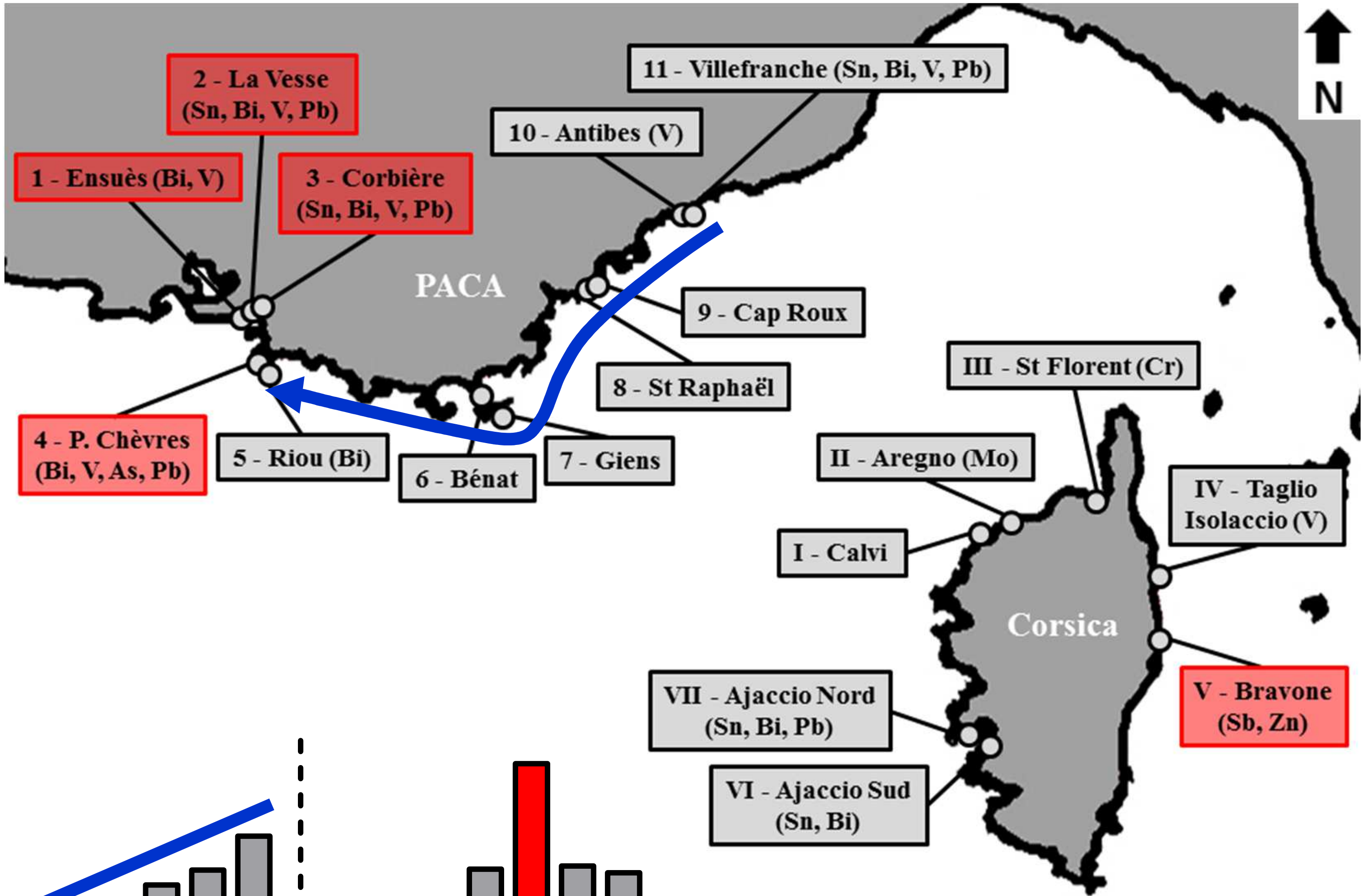
<u>Random list 1</u>:
Be, Al, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Mo, Ag, Cd, Sn, Sb, Pb, Bi

<u>Random list 5</u>:
Sb, V, Sn, Se, Be, Pb, Ni, Mo, Mn, Fe, Cu, Cr, Co, Cd, Bi, Zn, As, Ag, Al

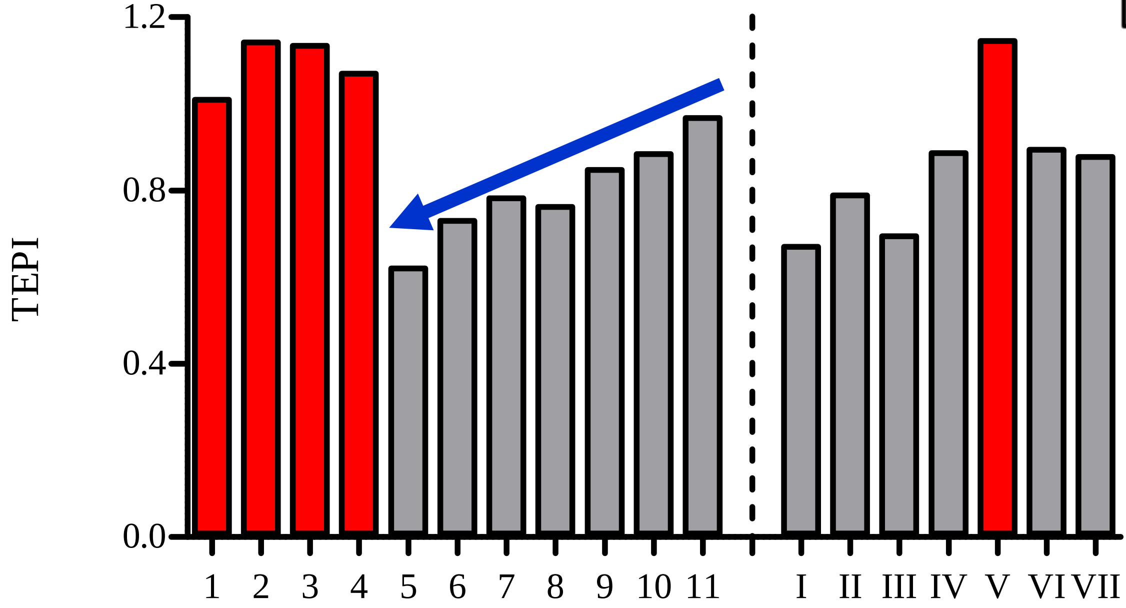




P. oceanica



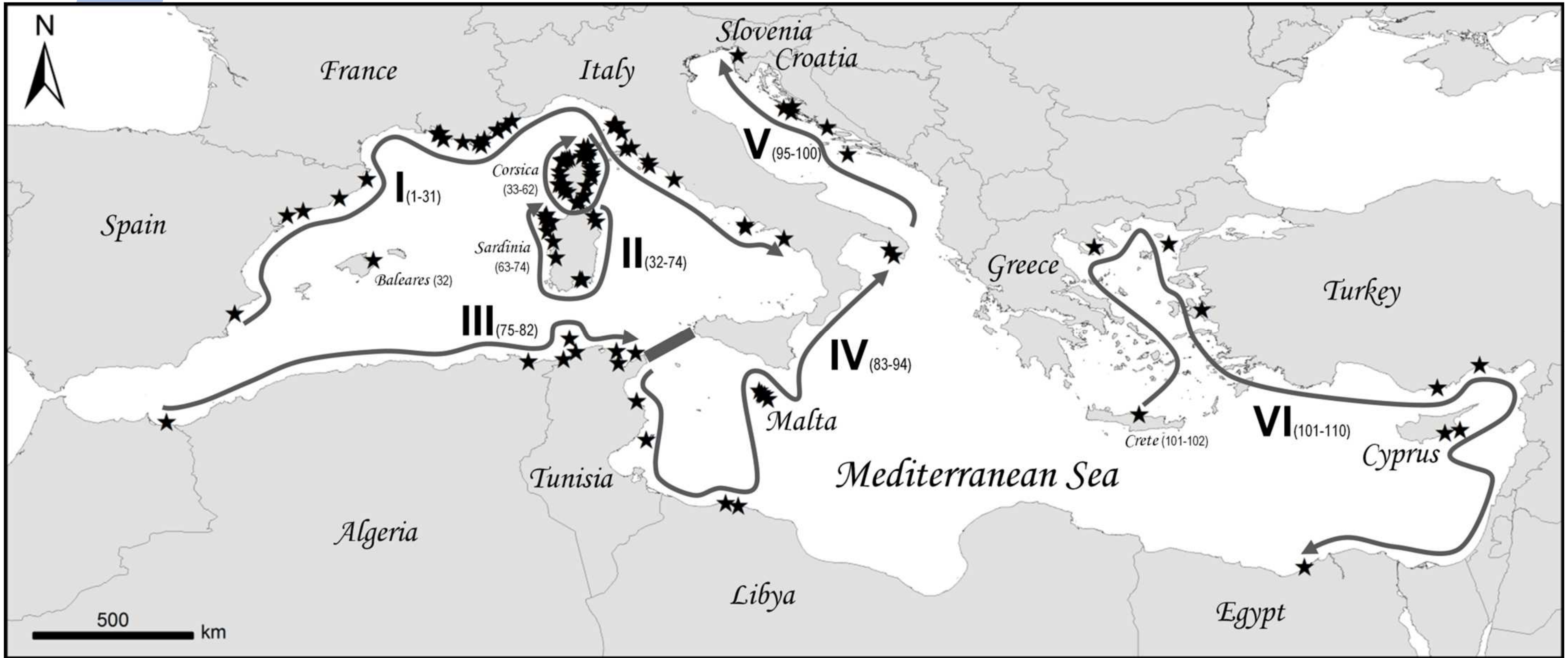
N
1 - Ensuès (Bi, V)
2 - La Vesse (Sn, Bi, V, Pb)
3 - Corbière (Sn, Bi, V, Pb)
4 - P. Chèvres (Bi, V, As, Pb)
5 - Riou (Bi)
6 - Bénat
7 - Giens
8 - St Raphaël
9 - Cap Roux
10 - Antibes (V)
11 - Villefranche (Sn, Bi, V, Pb)
PACA
I - Calvi
II - Aregno (Mo)
III - St Florent (Cr)
IV - Taglio Isolaccio (V)
V - Bravone (Sb, Zn)
VI - Ajaccio Sud (Sn, Bi)
VII - Ajaccio Nord (Sn, Bi, Pb)
Corsica



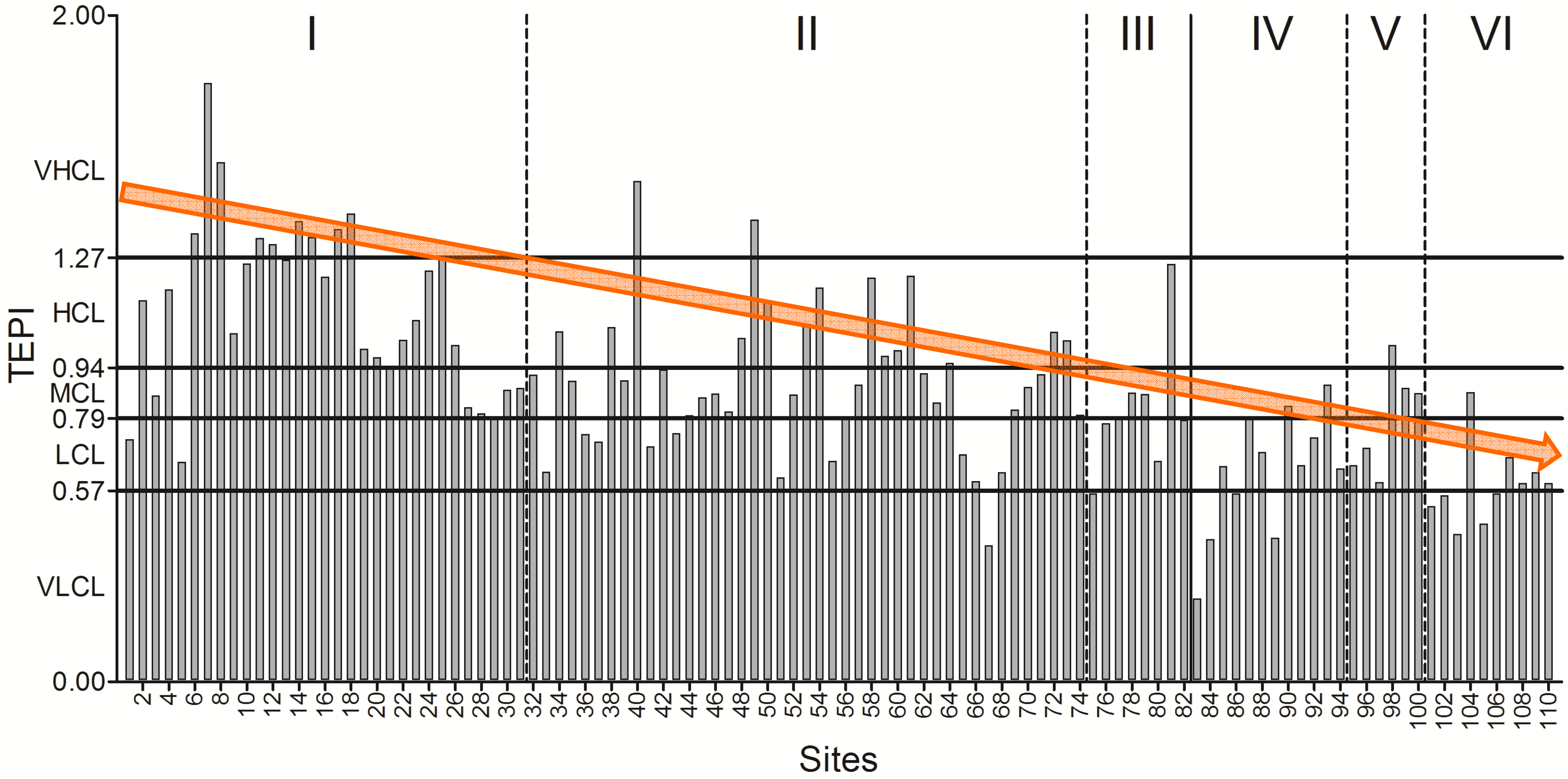
TEPI
1.2
0.8
0.4
0.0
1 2 3 4 5 6 7 8 9 10 11
I II III IV V VI VII

Sampling

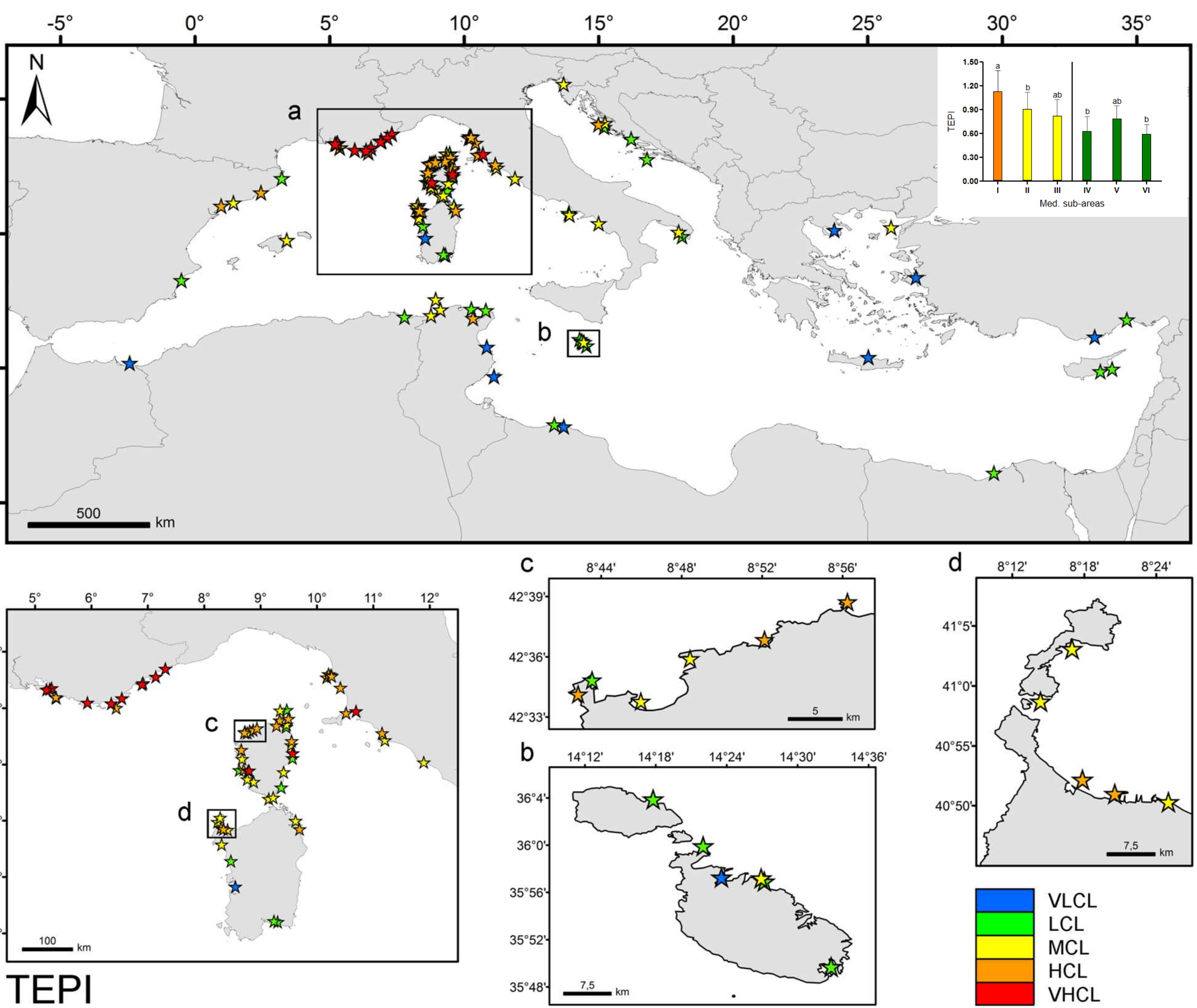
110 sites differing by their levels of exposure to contaminants sampled for *P. oceanica*.



Global contamination



RESULTS - DISCUSSION



TEPI

MATERIAL - METHODS

Maths and stats: monitoring

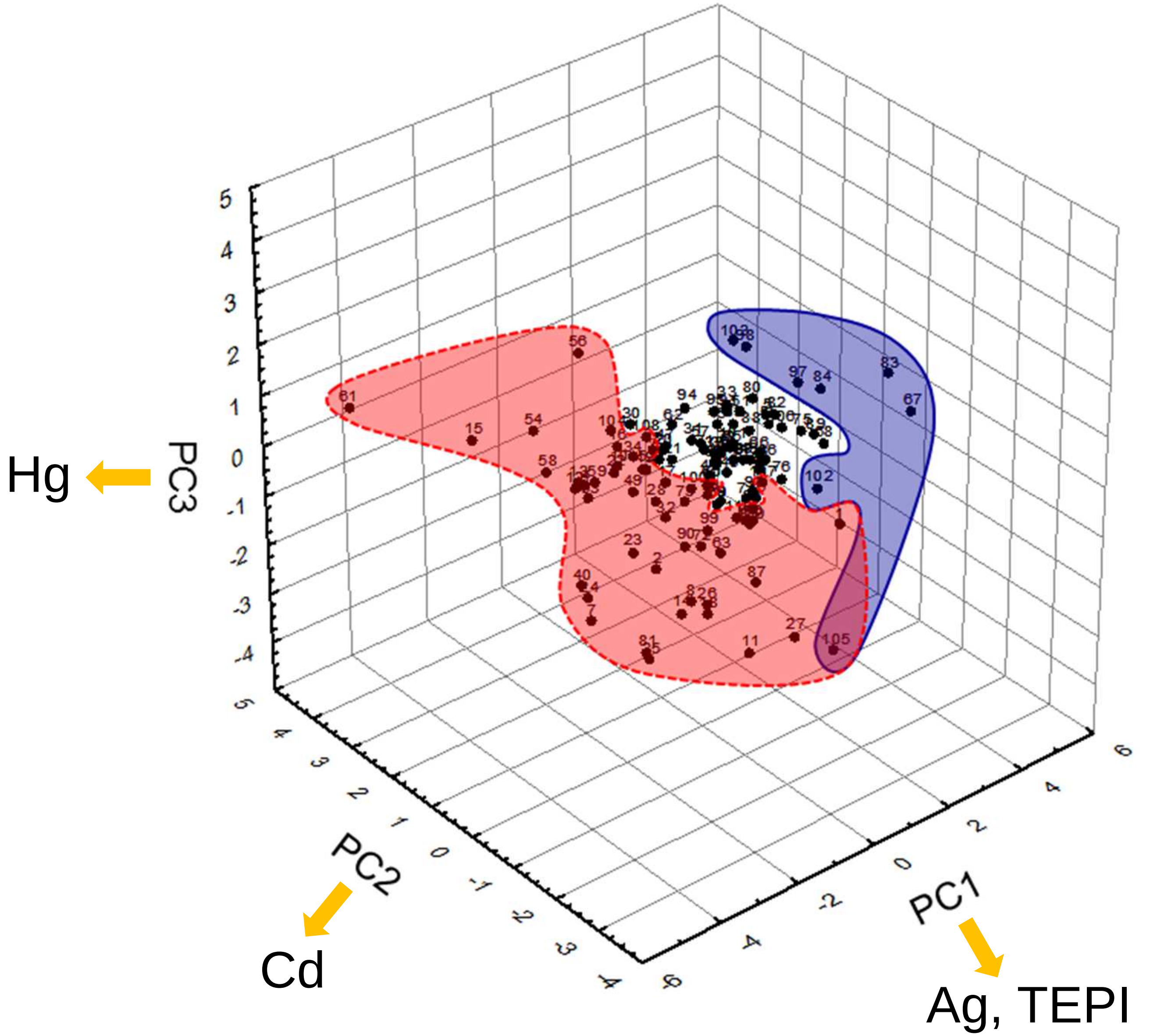
- Water quality scale
- Contamination indices:
  - Trace Element Spatial Variation Index (TESVI)
  - Trace Element Pollution Index (TEPI)

Maths and stats: spatial analysis

- GIS mapping
- Principal component analysis
- Cluster analysis
- Correlation analysis

Principal component analysis

R E S U L T S - D I S C U S S I O N



R E S U L T S - D I S C U S S I O N

Correlation analysis

	Ag	As	Cd	Cu	Hg	Ni	Pb	TEPI
Ag	1.000							
As	0.204	1.000						
Cd	**0.291**	-0.168	1.000					
Cu	**0.549**	0.096	0.084	1.000				
Hg	0.008	-0.074	-0.043	-0.047	1.000			
Ni	**0.464**	0.178	**0.625**	**0.425**	0.006	1.000		
Pb	**0.294**	**0.252**	0.110	**0.261**	-0.014	0.126	1.000	
TEPI	**0.777**	**0.512**	**0.383**	**0.539**	0.132	**0.686**	**0.518**	1.000

Correlation matrix of parametric Pearson's correlation coefficients and non-parametric Spearman's rank correlation coefficients between TE concentrations and TEPI values in *P. oceanica*. Correlations significant at $p < 0.05$ are in bold; correlations significant at $p < 0.01$ are in bold underlined.

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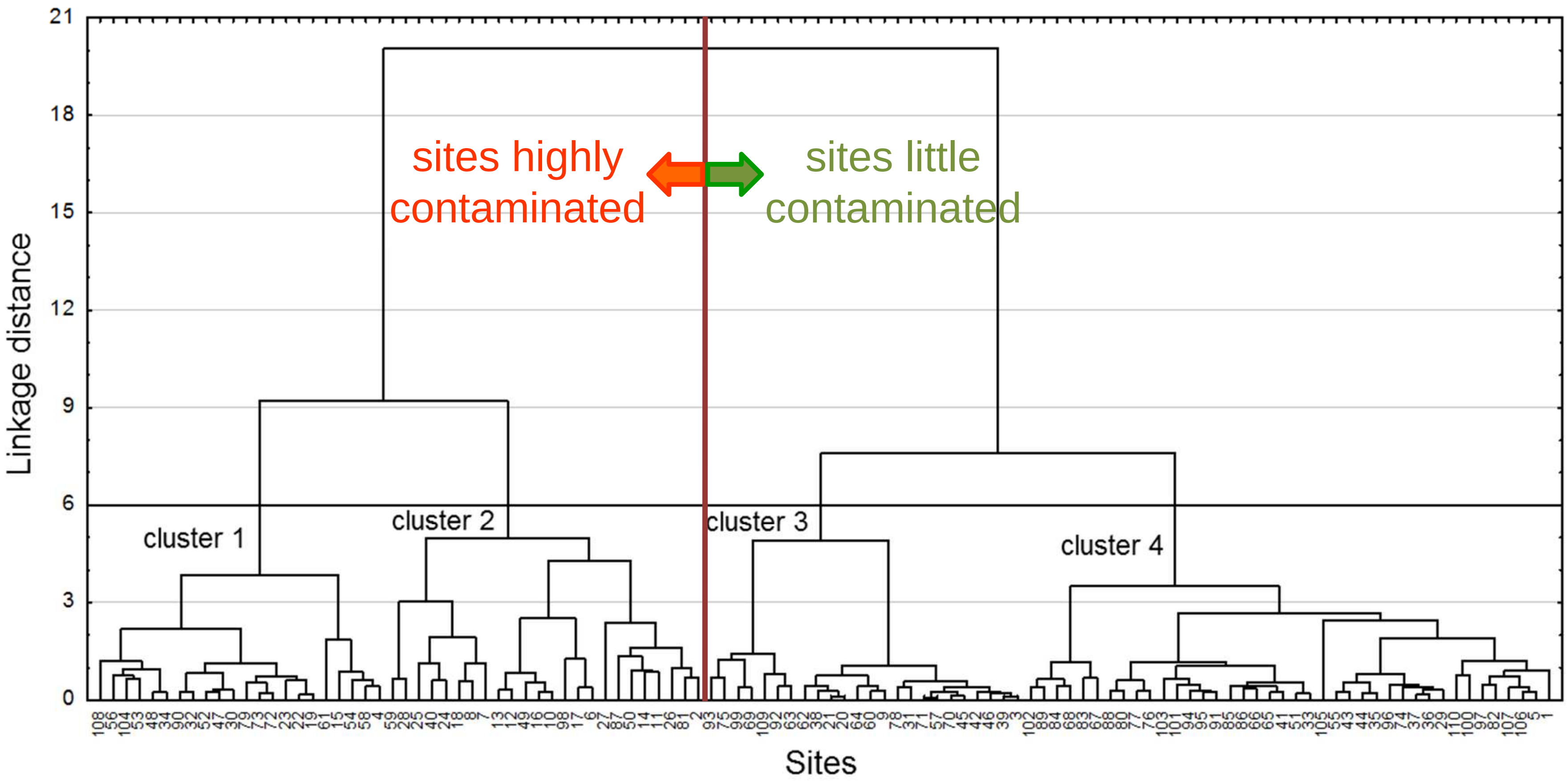
Cluster analysis



Dendrographic classification after cluster analysis of Ag, As, Cd, Cu, Hg, Ni and Pb concentrations measured in the blades of *Posidonia oceanica*, and TEPI values calculated from mean normalized TE concentrations.

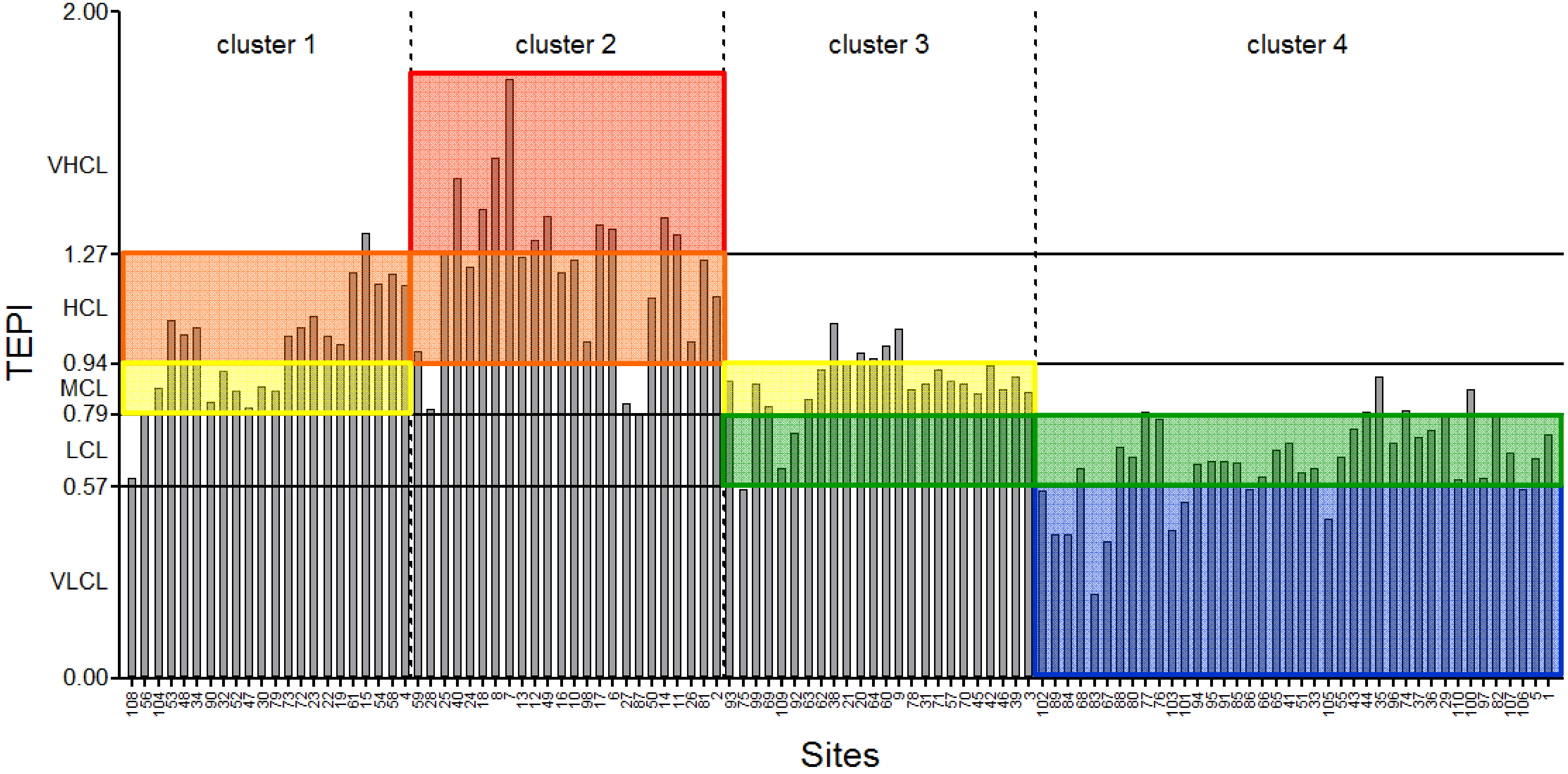
R E S U L T S - D I S C U S S I O N

Cluster analysis

HC by Cd, Ni; LC by As

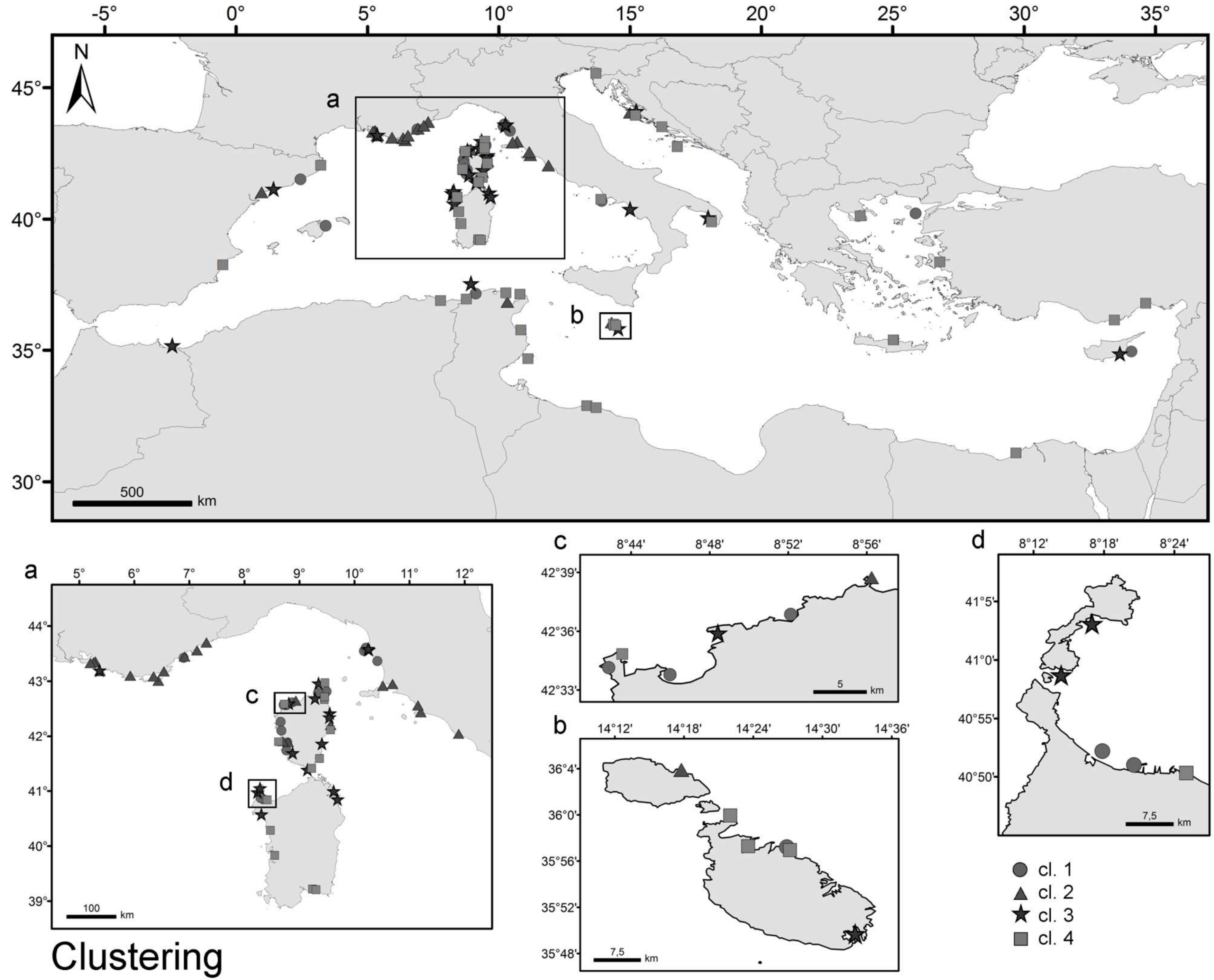
HC by Ag, As, Pb

LC by TEs overall



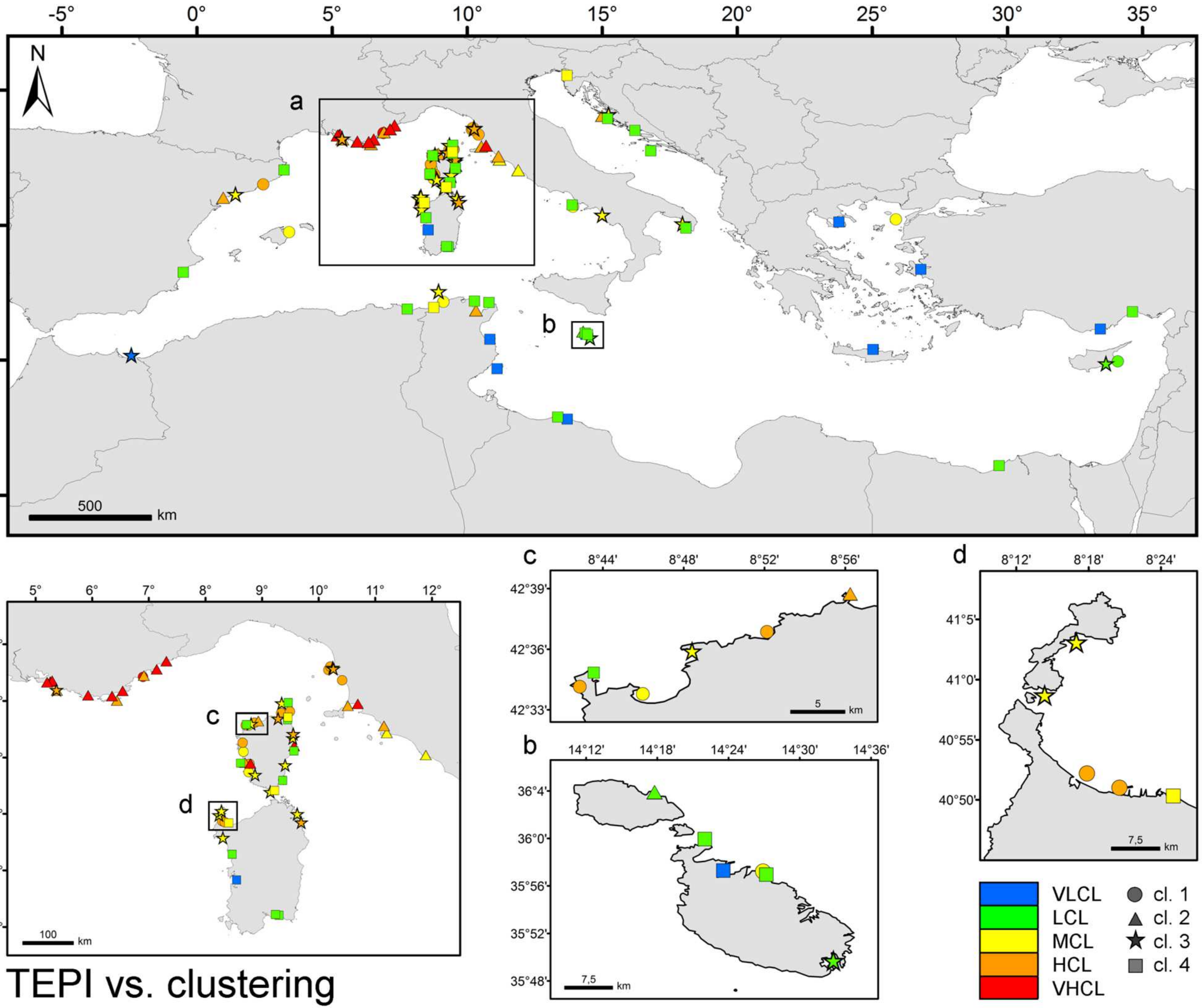
TEPI values calculated from mean normalized Ag, As, Cd, Cu, Hg, Ni and Pb concentrations measured in the blades of *P. oceanica* adult leaves. Sampling sites are sorted on the graph according to the dendrographic classification after cluster analysis of trace element concentrations and TEPI values.

RESULTS - DISCUSSION



Clustering

R E S U L T S - D I S C U S S I O N



TEPI vs. clustering

Conclusion

CONCLUSION

Sustainable coastal management requires the development of appropriate **contamination classification systems**.

→ Combined utilization of several **complementary monitoring tools**:

- water quality scale;
- pollution index (TEPI and TESVI);
- spatial analysis (PCA, CA, correlation analysis and GIS mapping).

In the Mediterranean:

- To assess TE contamination threats;
- To depict contamination gradients;
- To monitor TE contamination at regional or local scales.

Conclusion: to privilege such **holistic approach**es to accurately monitor the TE contamination rate of coastal waters and to transfer **relevant information** on this **composite problem** to environmental managers and policy makers.

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Bioassessment of trace element contamination of Mediterranean coastal waters using the seagrass *Posidonia oceanica*

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