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Conflicting outcomes of integrated approach for sediment quality assessment in Sardinian coastal area subjected to mining activities

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Environmental characterization of sediments from marine coastal area affected by heavy metal contamination due to past intense mining activity applying an integrated approach which took into account

– physical characteristics (**grain-size, mineralogy**)

– chemical parameters (**total concentration and sequential extraction**)

– ecotoxicological study (**bioassays on species at different level in trophic chain**)

Aim of the work

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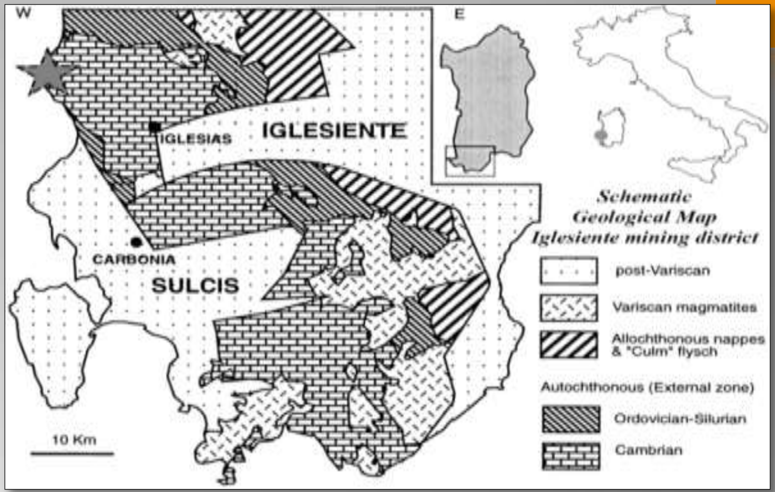

Sardinia, part of southern European plate, is mainly characterized by Paleozoic (Lower Cambrian to Lower Permian) rocks deformed during the Hercynian orogenesis, overlaid by Mesozoic rocks.

In the study area, located in the SW Sardinia, the meta-sedimentary rocks dominate the bedrock along the coast. Meta-sandstones and claystones with minor limestone lenses are capped by a thick carbonate succession which **hosts the major mineralization of the Sulcis Iglesiente mine district**.

Geological framework

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Study area

Over 40 mines exploited mainly **galena (PbS)** and **sphalerite [(Zn,Fe)S]** for about 150 years until 1990s. Also evidence of mining activity since the Roman age was found.

This intensive mining activity **left on site a large volume of mine residues** which are **still subjected to processes of weathering** strongly **impacting coastal marine sediments** of the study area.

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Previous studies on the marine area facing the mine district highlighted **exclusively sandy sediments** with local presence of gravelly levels; modest percentages of fine fraction are only locally present. The **mineralogical composition reflects the types of outcropping rocks** associated with processing residues deriving from exploiting activities.

Environmental status (1/3)

The chemical analyzes recognized in the superficial sediments very high concentrations of

– **Zn (57 - 42,764 mg kg^{-1})**
– **Cd (0.16 - 164 mg kg^{-1})**
– **Pb (17.2 - 3,423 mg kg^{-1})**

over the whole area with a decreasing pattern along depth.

Locally, significant concentrations of

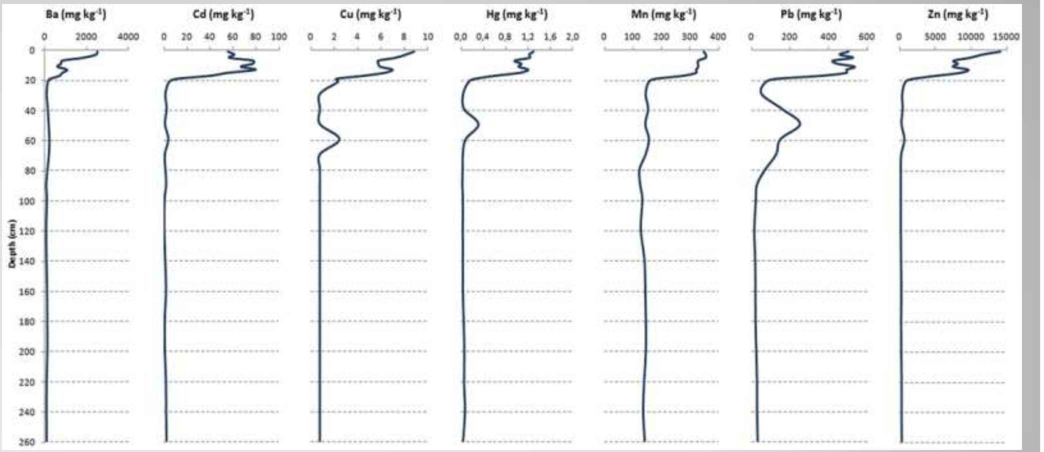
– **As (9 - 72 mg kg^{-1})**
– **Hg (< 0.05 - 12 mg kg^{-1})**

were recorded, mainly located in deeper levels. *ISPRA, 2015*

Environmental status (2/3)

The study of **sediment cores** showed concentration profiles typical of areas affected by **anthropogenic enrichment**, with higher and variable concentrations in the superficial levels and a significant reduction, with steady values, in the underlying levels.

The **background values**, determined on the deeper levels of the core, allowed to **discriminate natural** metal contribution **from the anthropogenic** one.



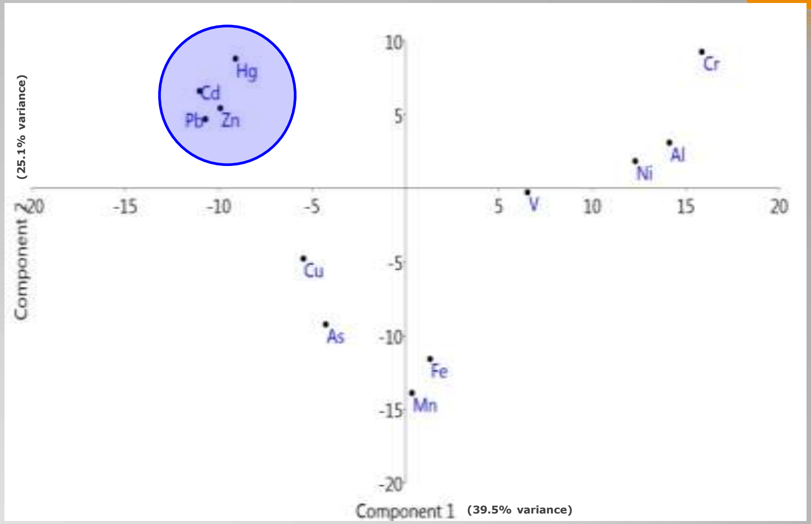
	As (mg kg-1)	Ba (mg kg-1)	Cd (mg kg-1)	Cr (mg kg-1)	Cu (mg kg-1)	Fe (%)	Hg (mg kg-1)	Mn (mg kg-1)	Ni (mg kg-1)	Pb (mg kg-1)	Zn (mg kg-1)
Mean natural	23.26	119	1.56	6.24	0.75	0.56	0.05	140	1.30	49	215
SD	2.55	45	0.65	1.12	0.00	0.04	0.07	10	0.96	41	73
BGV	**28.4**	**209**	**2.90**	**8.5**	**0.75**	**0.65**	**0.20**	**160**	**3.2**	**131**	**361**
EQS	**12**		**0.30**	**50**			**0.30**		**30**	**30**	

Romano et al., 2017. Marine Pollution Bulletin 122, 331–343

Environmental status (3/3)

Cd, Hg, Pb and Zn, compared with local background values and distribution and highlighted by PCA, can be recognized of anthropogenic origin and derived from the mine district.

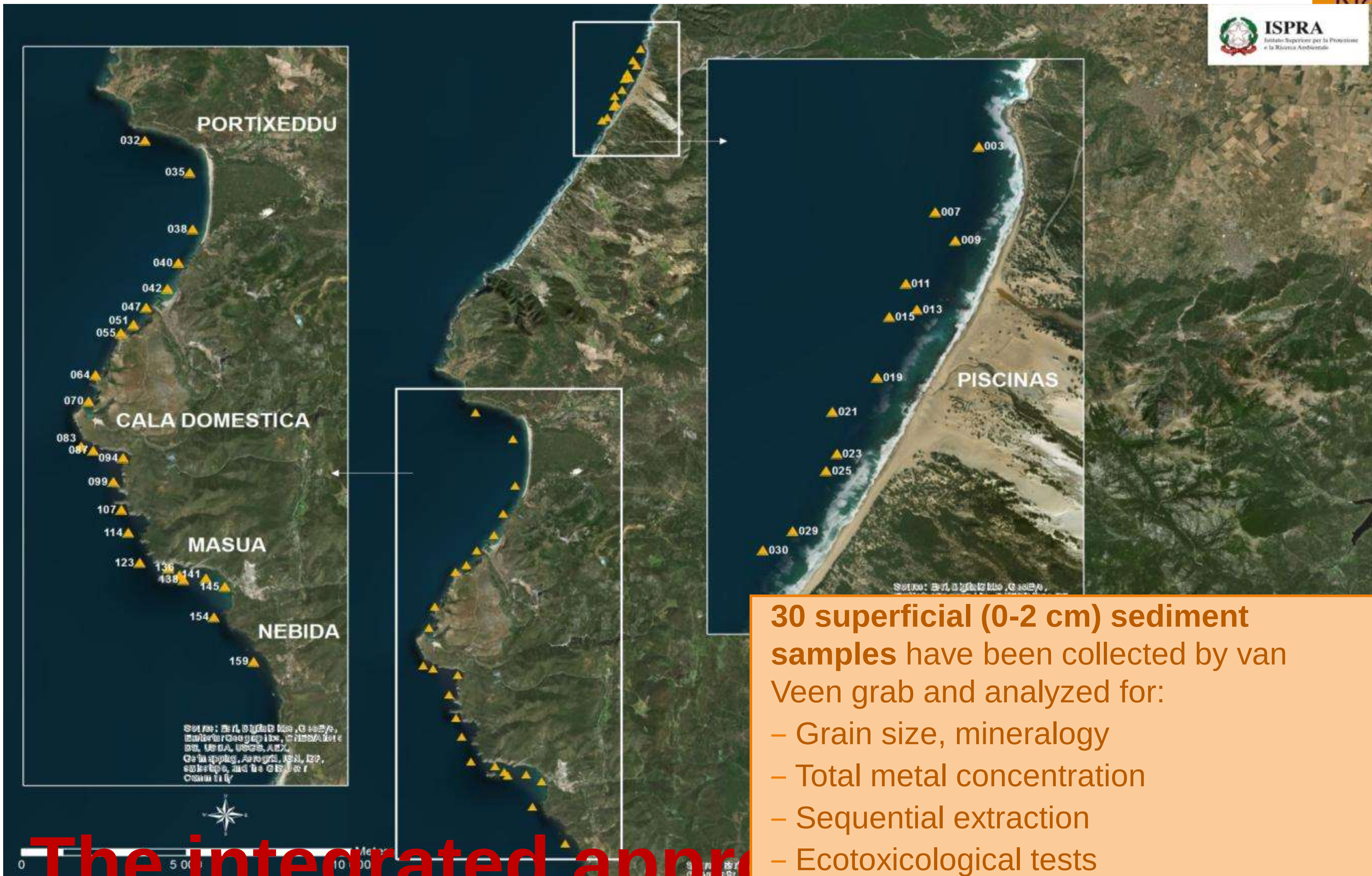
This also in accordance with Cidu (2007) who found high Hg, Pb and Zn in groundwater of abandoned mine sites of the area



Cidu, 2007. Mine Water Environment 26, 88-101

	Al	As	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Pb	V	Zn
MINIMUM	1123	5,0	0,2	2,5	0,5	3246	0.03	79	1.2	14	5,4	57
Q 1	2601	14,9	1,2	2,5	0,5	5030	0.11	136	2.6	53	10,6	180
MEDIAN	3226	17,6	**3.8**	5,8	**1,9**	5787	**0.29**	**170**	3.2	**120**	12.0	**564**
Q 3	4062	20,9	**16.0**	6,4	**4,5**	7461	**0.66**	**308**	**3.8**	**278**	14.9	**2073**
MAXIMUM	31164	**72,.0**	**260.6**	**42,1**	**96,4**	**95337**	**12.00**	**5238**	**27.0**	**3424**	48.0	**42764**
LOCAL BACKGROUND	**n.d.**	**28.4**	**2.9**	**8.48**	**0.75**	**6500**	**0,20**	**160**	**3,2**	**131**	**n.d.**	**361**

Environmental evidence



30 superficial (0-2 cm) sediment samples have been collected by van Veen grab and analyzed for:

- Grain size, mineralogy
- Total metal concentration
- Sequential extraction
- Ecotoxicological tests

The integrated approach – methods (1/3)

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- ***Grain size*** (Romano et al. 2009)
  - Analyses by sieving and laser granulometer
- ***Total metal concentration*** (ISO 11466)
  - Cd, Pb, Zn by ICP-AES (EPA 7131A, EPA 6010b)
  - Hg by Direct Mercury Analyzer (EPA 7473)
- ***Sequential extraction*** (Campanella et al. 1995)
  - 1st fraction: both physically adsorbed and linked to carbonates metals
  - 2nd fraction: metals linked to the iron and manganese oxides
  - 3rd fraction: separation of humic material from the bulk;
  - 4th fraction: extraction of humic material by soda;
  - 5th fraction: remaining organic matter and sulphides.
- ***Ecotoxicological tests***
  - *Vibrio fischeri* – sediment/elutriate **ICRAM 2003/APAT-IRSA29/2003**
  - *Dunaliella tertiolecta* - elutriate **UNI EN ISO 10253 modified**
  - *Brachionus plicatilis* - elutriate **ASTM E 1440-1491**

The integrated approach – methods (2/3)

The integrated approach – methods (3/3)

Ecotoxicological bioassays set

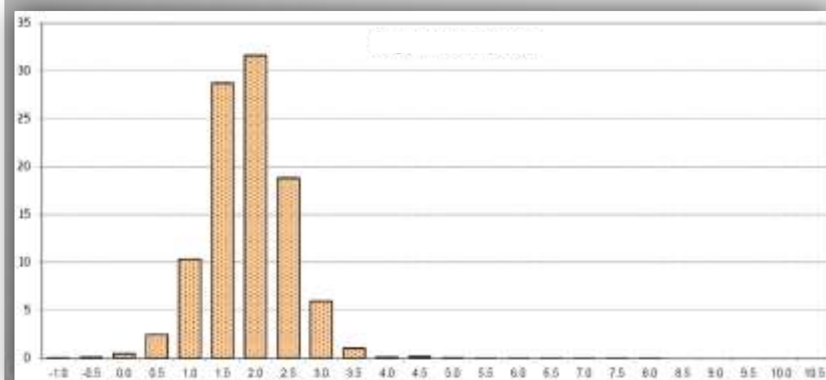
Bioassays have been selected according to National Guidelines

Three test species belonging to different taxonomic groups:

- at least one to be applied to the solid phase of the sediment
- at least one to be applied to the liquid phase (elutriate)
- the list of species that can be used is the following:
  - **algae *(Dunaliella tertiolecta)***
  - **bacteria *(Vibrio fischeri)***
  - **rotifer *(Brachionus plicatilis)***
  - mollusc
  - crustacean

Grain size: The sediments are predominantly sandy, ranging **from medium to fine and very fine sands**. Gravel and /or pelitic fraction is very scarce. The distribution curves generally have a unimodal trend.

Mineralogy: prevalence of quartz with feldspar, biotite, sporadic vulcanites, calcite and mining residues. In the finer fractions, pyroxenes, amphiboles, garnets, magnetite, ilmenite, pyrite and bioclasts.



The integrated approach - results (1/10)

The Enrichment Factor, determined for **Cd**, **Hg**, **Pb** and **Zn** using local background levels, was **from minor to severe**

EF> 50 extremely severe enrichment

25 ≤ EF ≤ 50 very severe enrichment

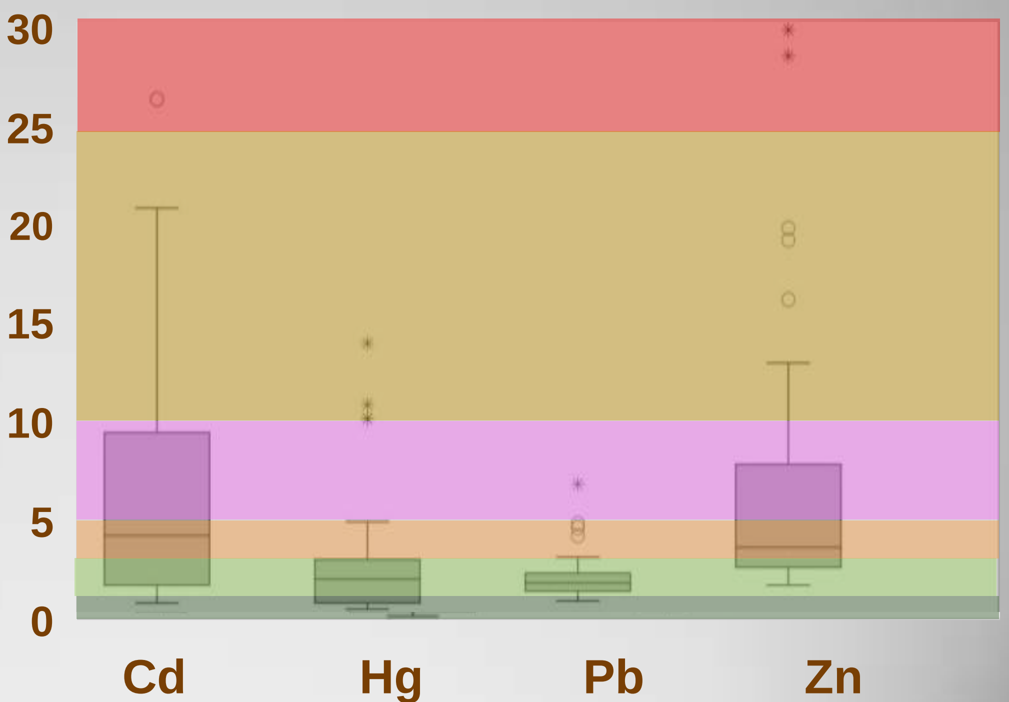
10 ≤ EF ≤ 25 severe enrichment

5 ≤ EF ≤ 10 moderate/severe enrichment

3 ≤ EF ≤ 5 moderate enrichment

1 < EF < 3 minor enrichment

EF< 1 no enrichment



(Birch & Olmos, 2008, ICES J. Mar. Sci. 65, 1407–1413)

approach - results (2/10)

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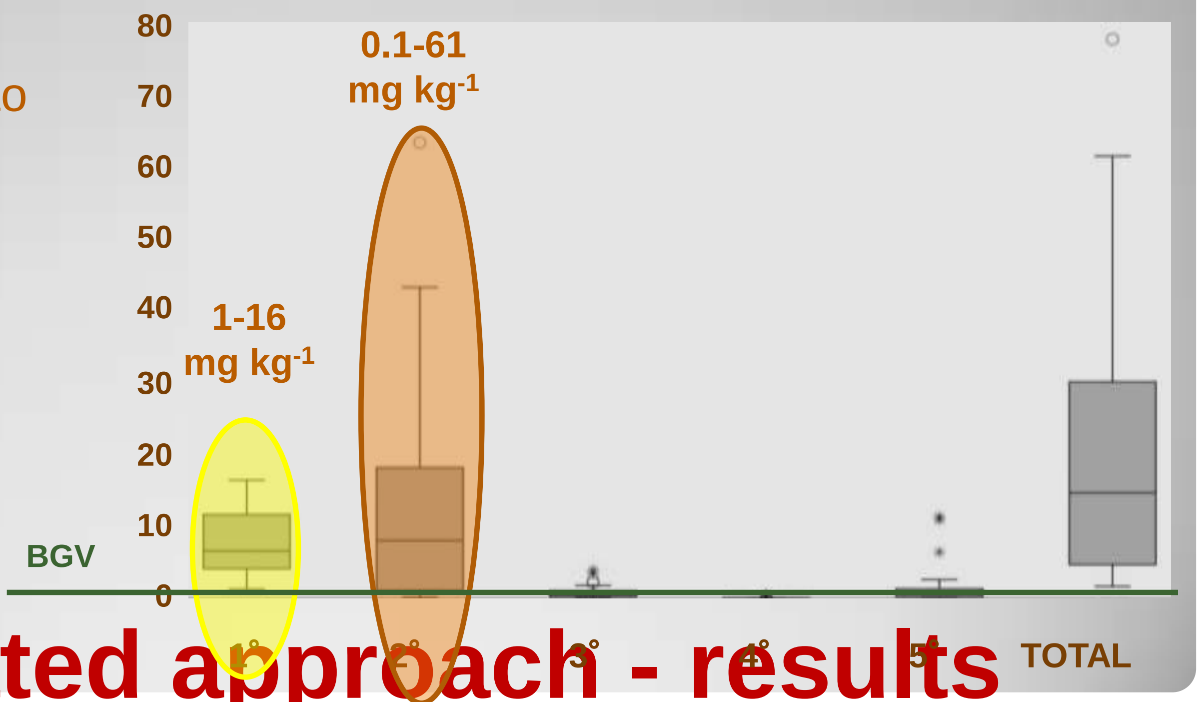
Sequential extraction (Cd)

1st step, physically adsorbed and linked to carbonates metals: **15 - 87%**

To **a higher total content** of Cd corresponds **lower extracted %** and vice versa

2nd step, fraction linked to Fe-Mn oxides: **6 – 81%**

The extracted concentrations in other steps are generally negligible, with a major contribution in the last step (sulphides).



The integrated approach - results (3/10)

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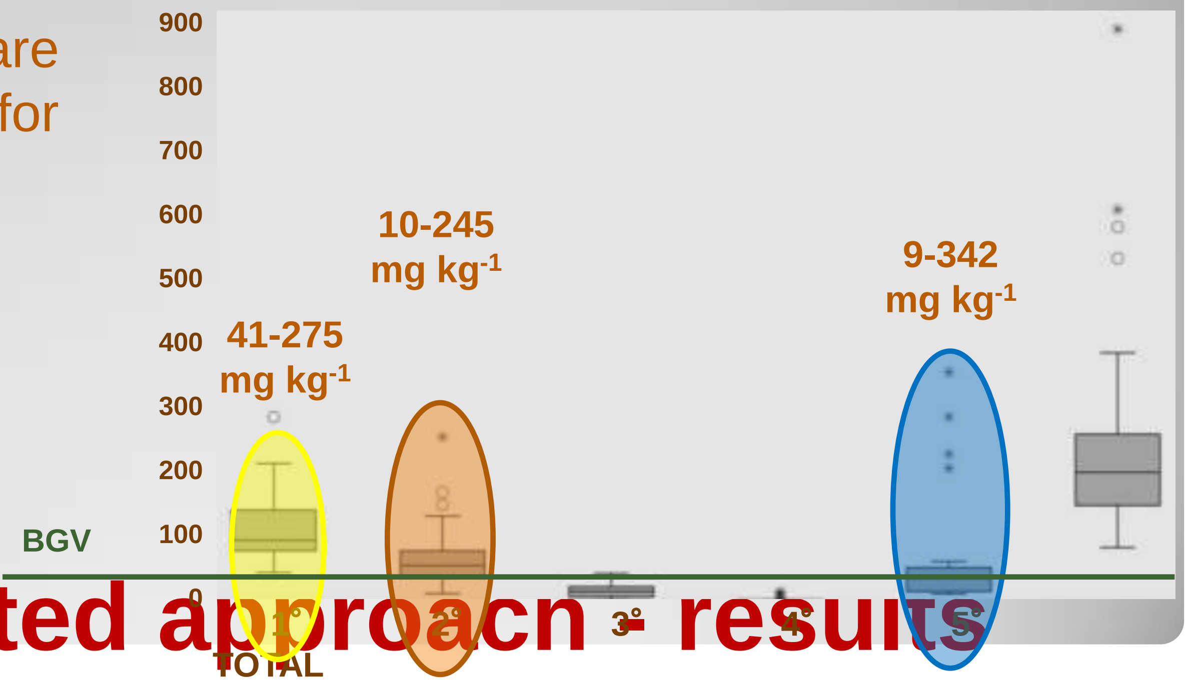
Sequential extraction (Pb)

1st step, physically adsorbed and linked to carbonates metals: **26-72%**

2nd step, fraction linked to Fe-Mn oxides: **11 – 39%**

The followings steps are not significant except for the last one (**6-49%**)



The integrated approach - results (4/10)

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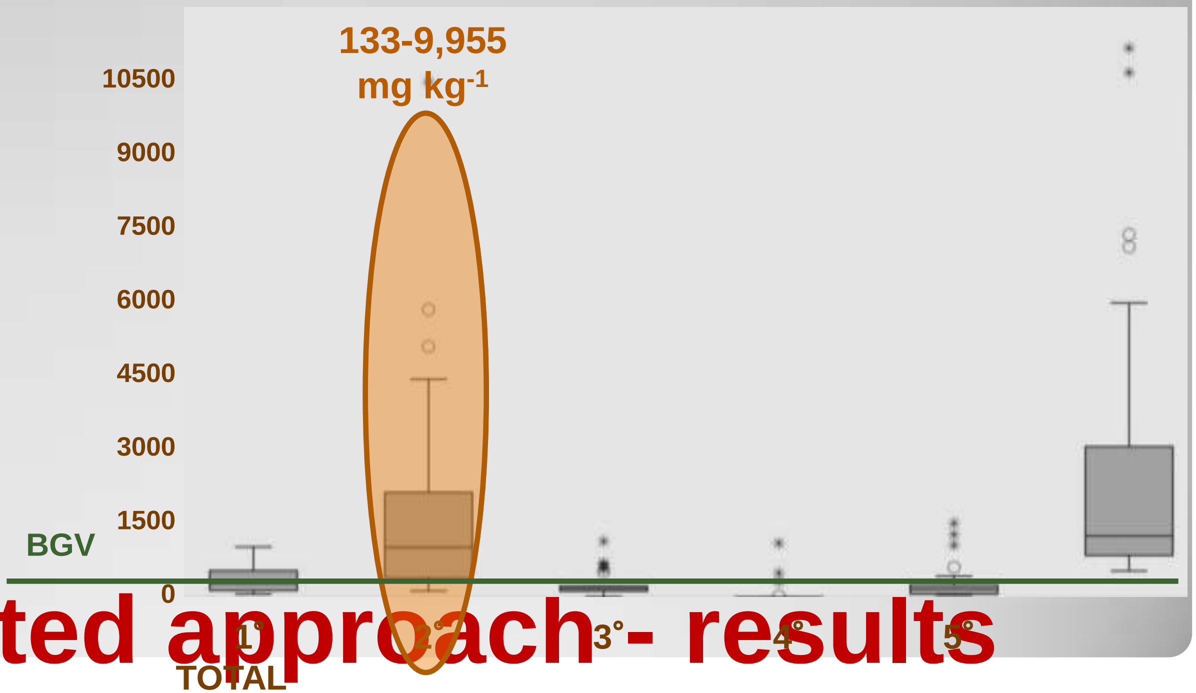
Sequential extraction (Zn)

Only 2nd step, fraction linked to Fe-Mn oxides, is the most important (**22 –99%**)

The extracted concentrations in other steps are generally negligible as percentages but not as concentrations



The integrated approach - results (5/10)

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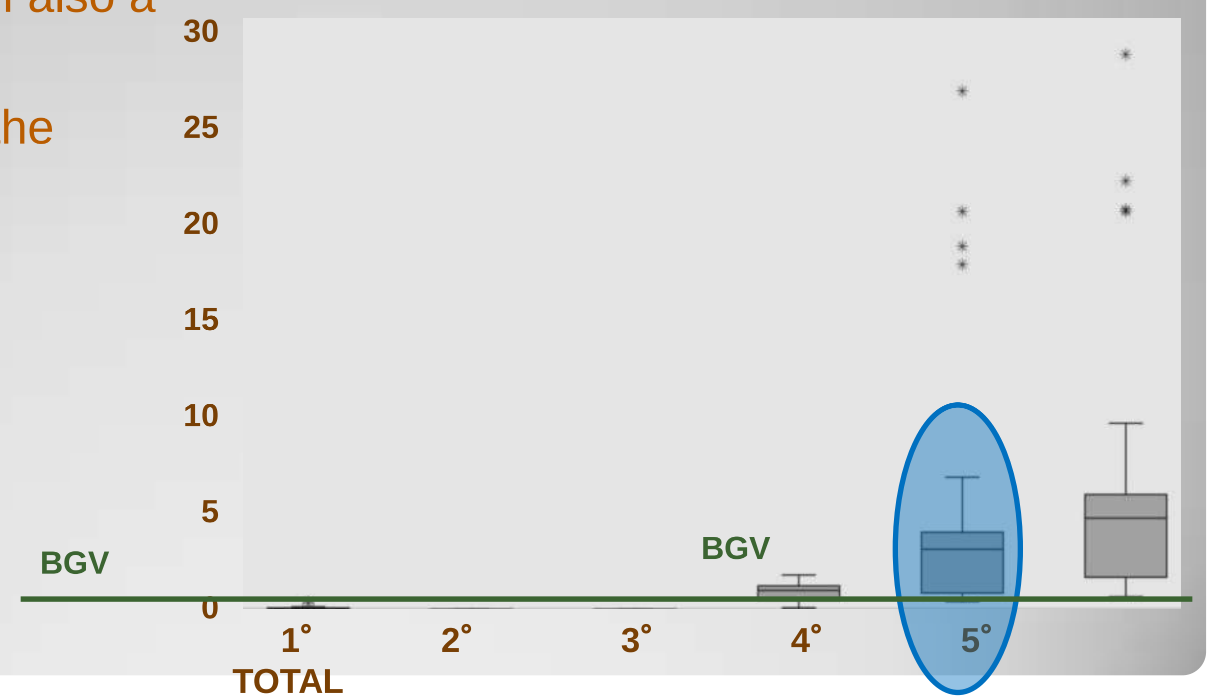
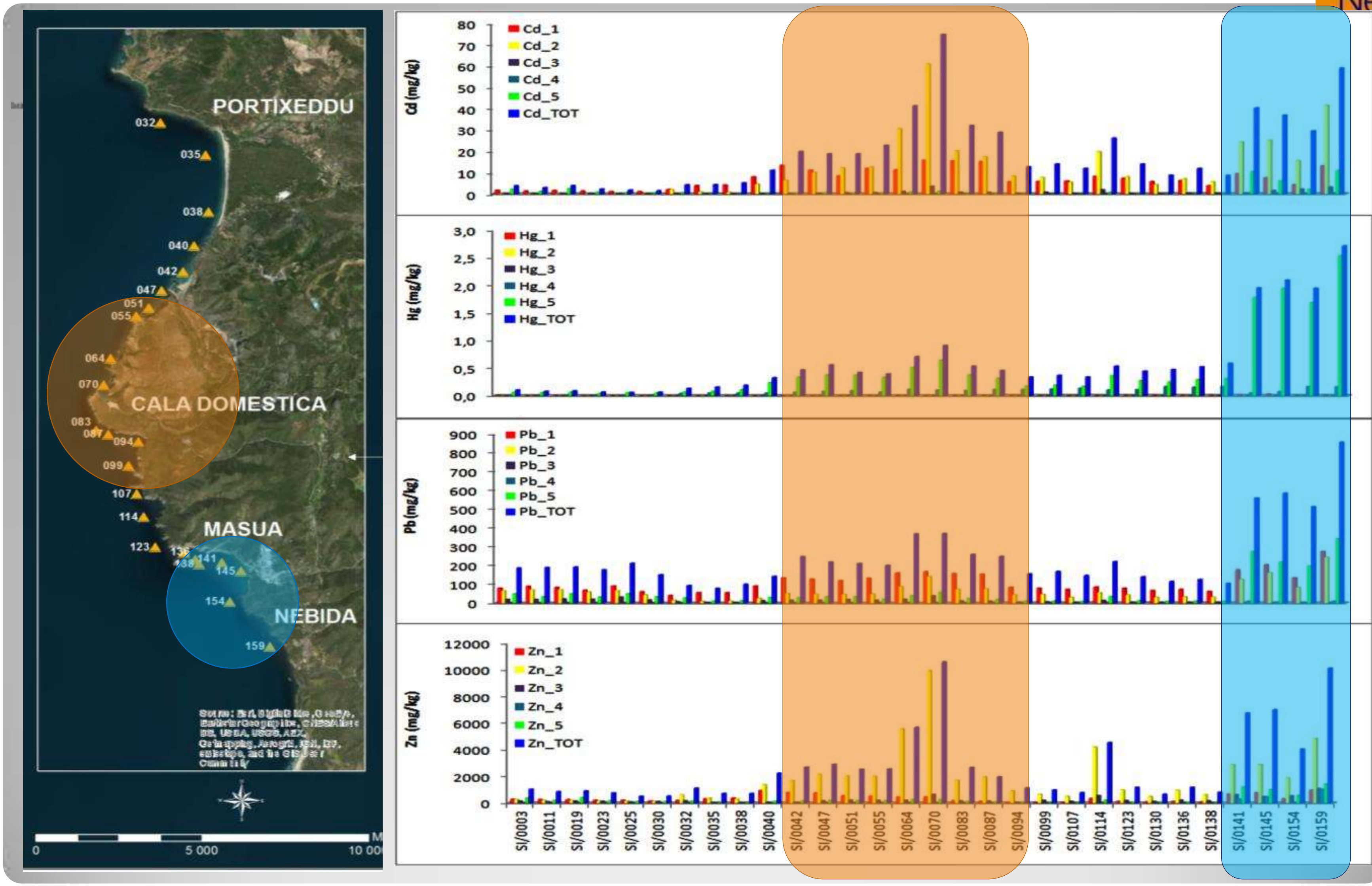
Sequential extraction (Hg)

The behavior of Hg is completely different from other metals.

It is mainly distributed in the last phase (**sulfide-related fraction and in the insoluble residue)**, with also a significant contribution of the fraction linked to the humic matter (4th step)



The integrated approach - results (6/10)



The integrated approach - results (7/10)

Toxicity class according to the species used

specie-test	eutrophic effect	CLASS A Absent or negligible toxicity	CLASS B Medium toxicity	CLASS C High toxicity	CLASS D Very high toxicity
Vibrio fischeri (sediment)		STI ≤ 3	3 > STI ≤ 6	6 > STI ≤ 12	STI > 12
Vibrio fischeri (elutriate)		EC_{50} > 100% EC_{20} ≥ 90%	EC_{50} ≥ 90% and EC_{20} < 90%	20% ≤ EC_{50} < 90%	EC50 < 20%
Brachionus plicatilis (elutriate)		EC_{20} 90% mortality < 20	EC_{50} > 100% and EC_{20} < 90%	40% ≤ EC_{50} < 100%	EC_{50} < 40%
Dunaliella tertiolecta (elutriate)	% biostimulation > 20	% inhibition /stimulation <20	% growth inhibition > 20		

APAT – ICRAM, 2007 (modified)

The results were expressed like:

Vibrio fischeri **–** sediment: S.T.I. (Sediment Toxicity Index), with application of the pelitic correction

Vibrio fischeri **–** elutriate: EC_{50}

Dunaliella tertiolecta: % of inhibition of algal growth

Brachionus plicatilis: % of mortality

The integrated approach - results (8/10)

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Results and toxicity class assigned

sample	*V. fischeri* (Solid Phase Test) S.T.I.	*V. fischeri* (elutriate) EC_{50}	*B. plicatilis* (elutriate) % mortality	*D.tertiolecta* (elutriate) % inhibition
SI/0003		>100	13	13.47
SI/0011	n.d.	>100	13	10.14
SI/0019	n.d.	>100	13	0.28
SI/0023	n.d.	>100	10	- 1.6
SI/0025	n.d.	>100	6.6	- 9.61
SI/0030	n.d.	>100	16.6	6.42
SI/0032	n.d.	>100	3	1.07
SI/0035	n.d.	>100	6.6	5.31
SI/0038	n.d.	>100	6.6	4.10
SI/0040	n.d.	>100	0	7.04
SI/0042	n.d.	>100	6.6	7.56
SI/0047	n.d.	>100	10	1.94
SI/0051	n.d.	>100	3	1.07
SI/0055	n.d.	>100	0	7.47
SI/0064	n.d.	>100	0	5.74

sample	*V. fischeri* (Solid Phase Test) S.T.I.	*V. fischeri* (elutriate) EC_{50}	*B. plicatilis* (elutriate) % mortality	*D.tertiolecta* (elutriate) % inhibition
SI/0070	n.d.	>100	0	- 1.27
SI/0083	n.d.	>100	10	7.76
SI/0087	n.d.	>100	3.33	7.47
SI/0094	n.d.	>100	3.33	5.39
SI/0099	n.d.	>100	3.33	6.20
SI/0102	n.d.	>100	3.33	5.49
SI/0107	n.d.	>100	6,67	3.91
SI/0114	n.d.	>100	10	-33.82
SI/0123	n.d.	>100	10	7.38
SI/0130	n.d.	>100	10	-4.68
SI/0136	n.d.	>100	10	6.16
SI/0138	n.d.	>100	3.33	-0.99
SI/0141	n.d.	>100	10	-24.49
SI/0145	n.d.	>100	3.33	17.89
SI/0154	n.d.	>100	0	-8.99
SI/0159	n.d.	>100	0	0.897

The integrated approach - results (9/10)

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Bioassay results

In all samples :

- *Vibrio fischeri* solid phase test **showed no toxicity** and it was not possible to detect values of STI;
- *Vibrio fischeri* elutriate test **showed no toxicity,** with EC50 > 100% and EC20 not calculable;
- *Brachionus plicatilis* test showed **no significant effect**, with mortality % < 20
- *Dunaliella tertiolecta* test showed **no significant toxicity** except for:
    - 6 samples with **light biostimulation**
    - 2 samples with **eutrophic effects**

The integrated approach - results (10/10)

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- The results of the **ecotoxicological tests did not provide indications on the toxicity** of these metals because they seem apparently inconsistent with respect to the magnitude of the total concentrations and the high mobility of these elements.
- Consequently, **they cannot replace the chemical-physical analyzes** and, in complex cases, they should have to be **combined with** determination of **bioaccumulation** of contaminants in marine organisms, **biomarker** and **benthic assemblages**

Take home message

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Thank you for your attention!

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