

MERCURY CONTAMINATION ON ITALIAN MARINE COASTAL AREAS DUE TO INDUSTRIAL AND MINING ACTIVITIES



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THE NATIONAL ROLE OF ISPRA Institute for Environmental Protection and Research

- ★ ISPRA came from the merge of different institutions like as marine research institute, wildlife research institute and environmental agency, collecting a wide technical and scientific proficiencies on environmental topics
- ★ ISPRA provides technical and scientific support, as well as necessary tools and know-how, for the environmental decision of the Italian Ministry of the Environment to safeguard the environmental and sustainable development paths agreed within the EU
- ★ ISPRA is actually the institutional and technical/scientific reference point for the whole country on environmental themes
- ★ ISPRA also represents a system's cohesion, while respecting local territories favoring a more homogeneous development of cooperation
- ★ ISPRA chairs the Federal Council of Agencies which belong to Environmental Agency System, a network which matches the knowledge of the territory and the local green problems with the prevention and national environmental protection policies

THE NATIONAL ROLE OF ISPRA

Department on the impacts on the marine environment

The Department on the impacts on the marine environment support the Public Administrations to make decision by means of its experience and knowledge gained on the whole issue of the sediment management carrying out experimental researches

The main research activities are focused on:

- ★ Definition of guidelines on marine environment (water, sediment, organisms)
- ★ Sediment quality assessment focused to their management taking in account the peculiarity of the area (reference and action levels)
- ★ Monitoring of sediment management, like as dredging or beach nourishment
- ★ Remediation of contaminated marine environments
- ★ Protection of marine habitats and biodiversity, monitoring the Marine Protected Areas (MPAs) and marine species

THE NATIONAL RELEVANCE CONTAMINATED SITES

National Relevance Contaminated Sites



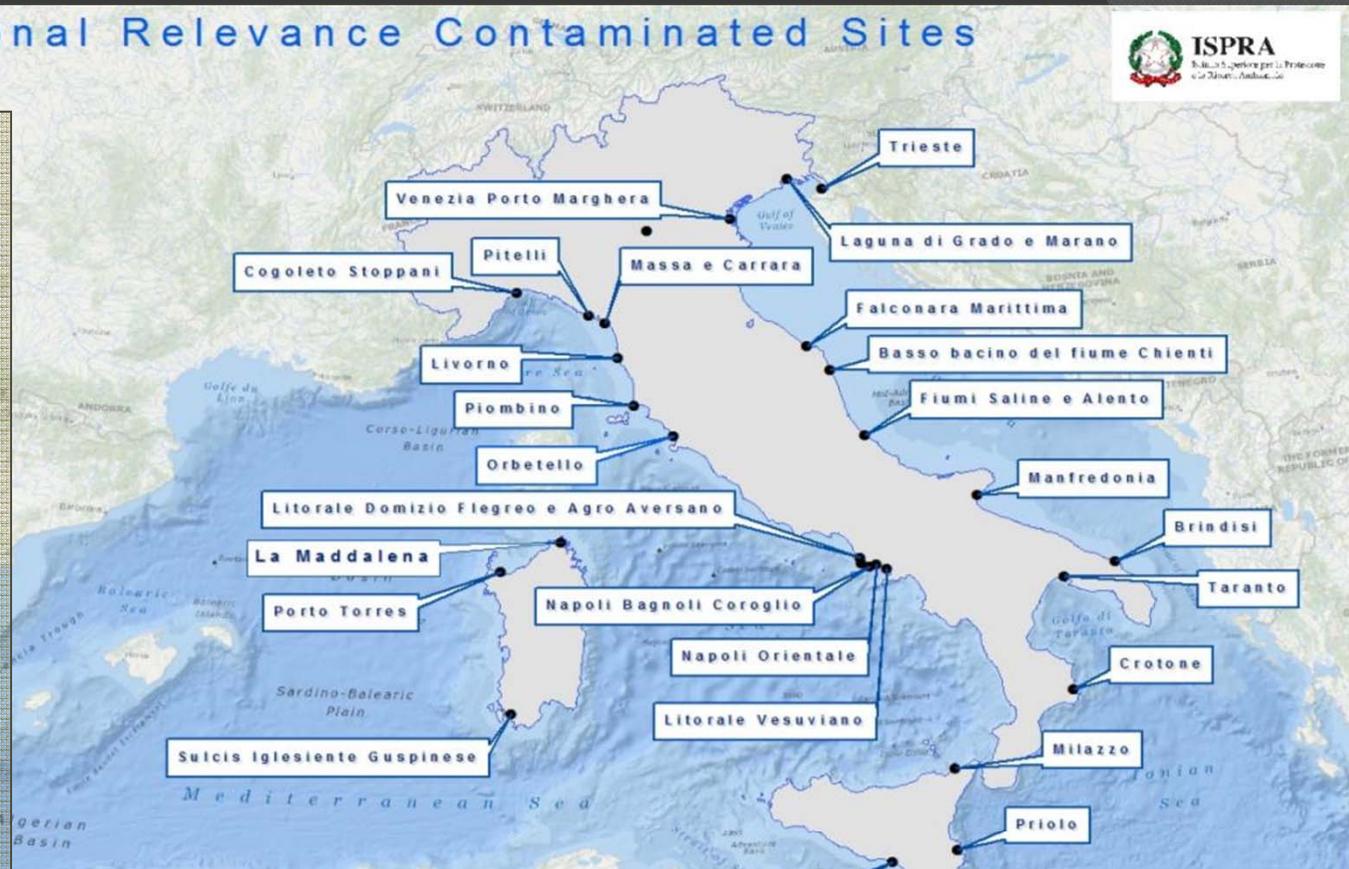
There are many human activities worked, or still working, along the Italian coastal areas, which determined an high pollution of the marine environment, like as chemical and / or petrochemical industries, harbor or military areas, urban, agricultural or mining settlement, etc.

Some national laws identified them as National Relevance Contaminated Sites (Laws 426/98, 388/2000, 179/2002) and Ministry of Environment defined specific processes for their remediation (Decreto n. 468/04).

ISPRA was then charged to define characterization strategies aimed to identify the appropriate operation for environmental clean up.

It was used an integrated approach (TRIAD approach) finalized to define the chemical-physical and ecotoxicological characteristic of marine areas. It was also studied the effect of contamination on marine organisms to evaluate the potential bioaccumulation on the food chain.

Finally, they were defined specific "values" for each site, based on chemical and ecotoxicological aspect, taking in account geochemical contribution, where present. They were useful for the evaluation of contamination of the areas



THE NATIONAL RELEVANCE CONTAMINATED SITES

The **RED** selected marine sites have been influenced by chlor-alkali plant and / or mining activities

National Relevance Contaminated Sites



THE ORBETELLO SITE

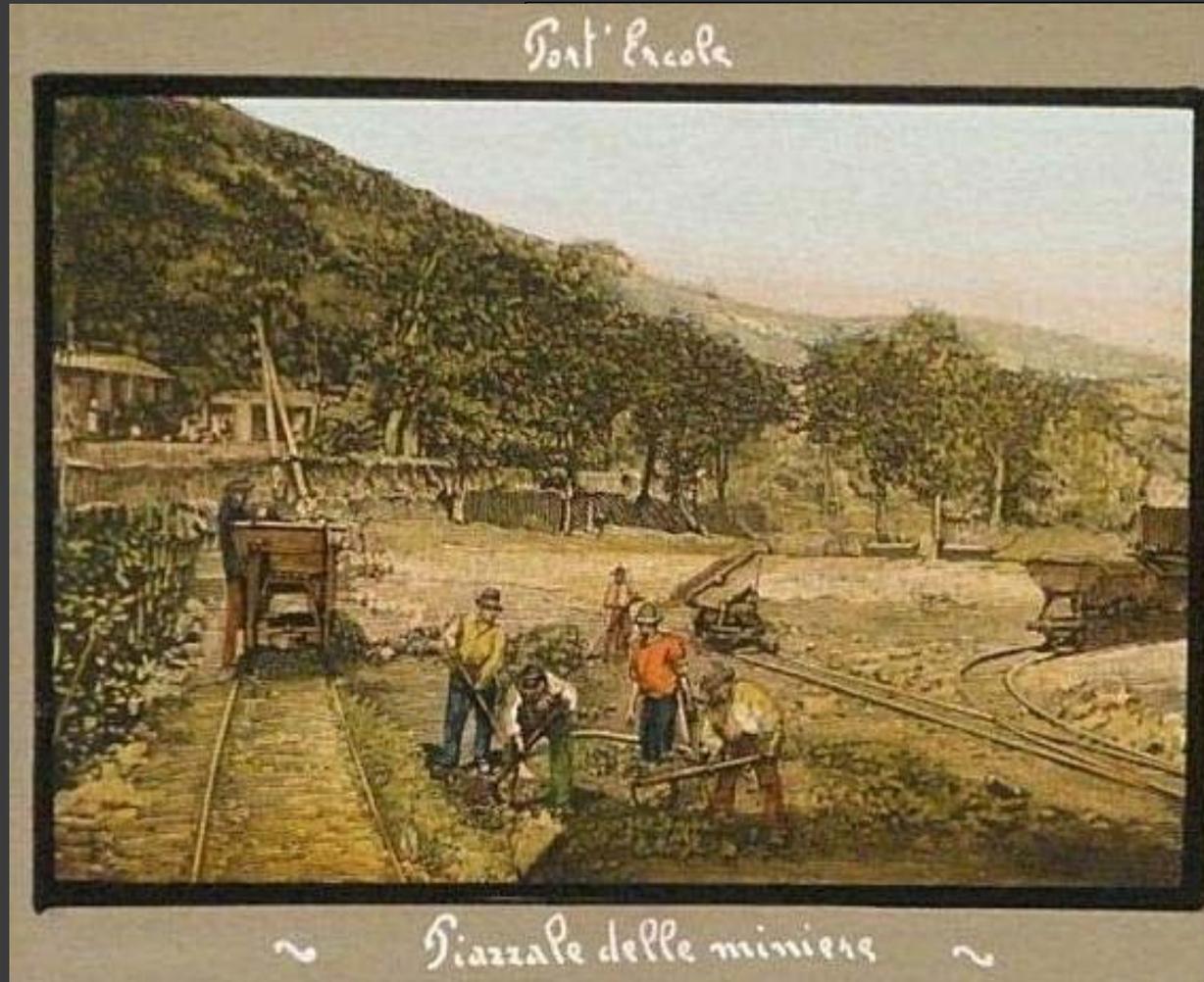


The Orbetello lagoon is an area of natural interest and it's included in Community Interest Sites. It's separated from the Tyrrhenian Sea by two tombolos that join the promontory of Monte Argentario to continental area and characterized by shallow water and scarce connection with open sea.

It's used for aquaculture plants and fishing of bass, bream, mullet and eels but it's also affected by anthropogenic impact which may be the source of environmental contamination, like as a mine worked in the past. Also *geological features* play an important role on the sediment geochemistry (Mt. Amiata mineralization)



THE ORBETELLO SITE – GEOLOGICAL FEATURES AND MINING ACTIVITIES



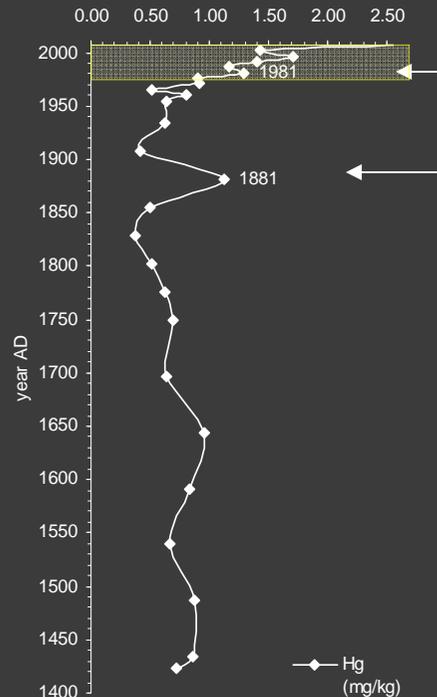
The area is interested by several mineralization sites but the most interesting is located in Terrarossa site, on the southern side of the Orbetello lagoon.

The mining extraction was active from 1873 until 1958, when stopped for the depletion of minerals.

The extraction method of *iron-manganese minerals* present in superficial site determined an high production of residual waste containing several metals, also including Hg, which were discharged directly in the lagoon

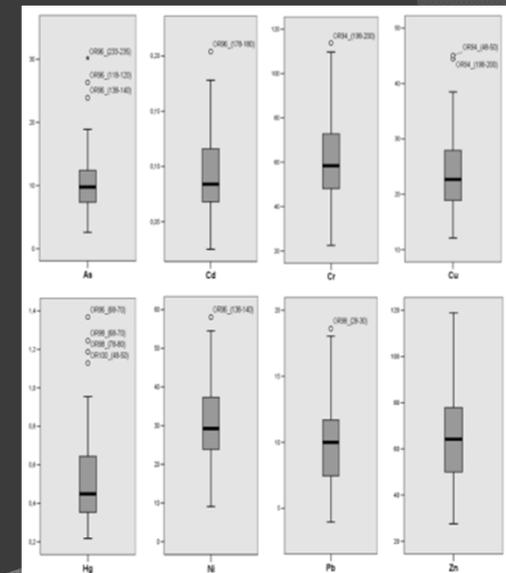
THE ORBETELLO SITE – LOCAL BACKGROUND VALUES

4 dated sediment cores were used for determination of local background values (BGV)
 All of them registered a sedimentation rate about 0.3 cm/y



MODERN ENRICHMENT (values not considered for BGV determination)

GEOCHEMICAL ANOMALY probably due to the onset of mining activity (eliminated from the database by means of box-plot technique)



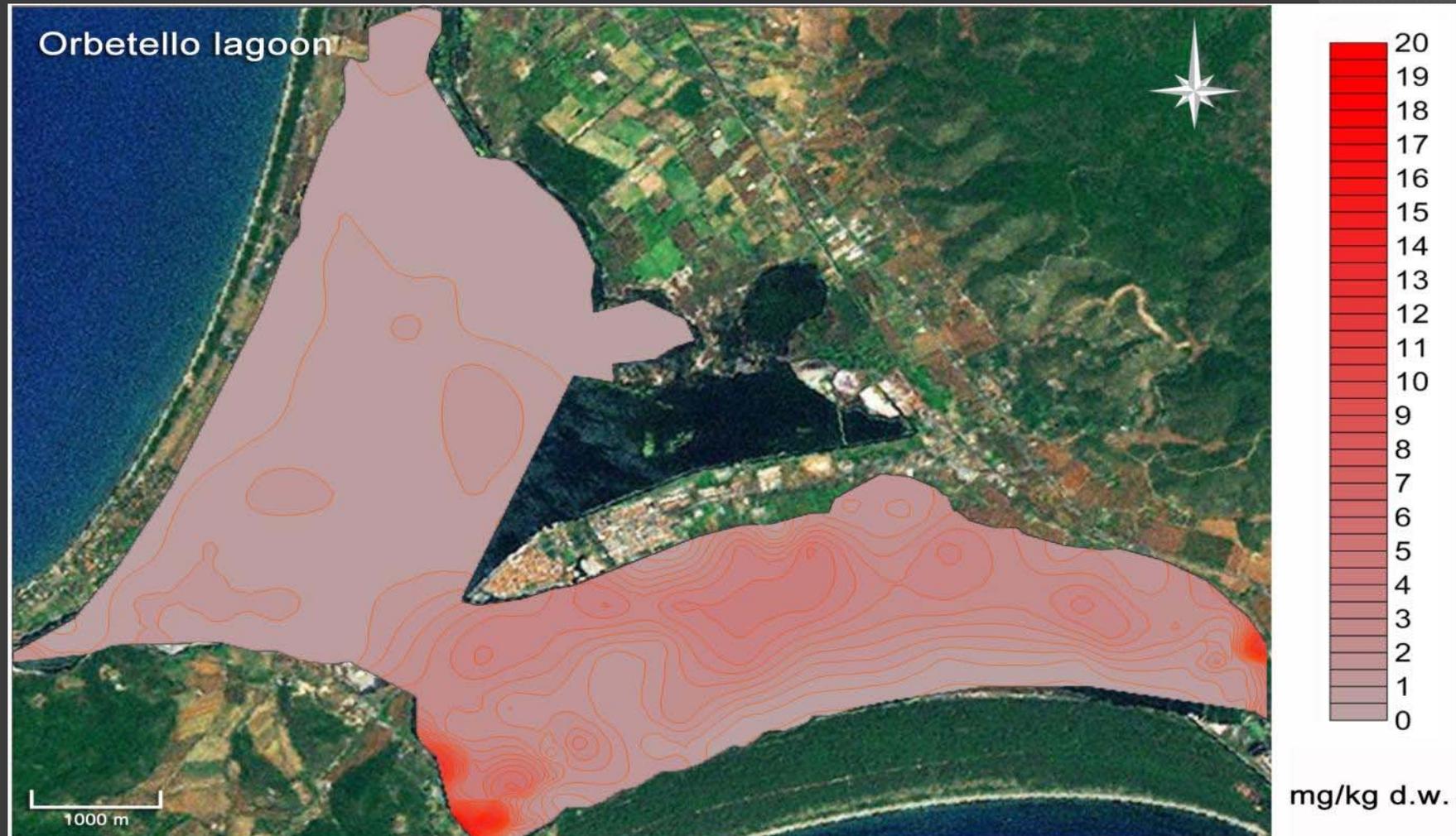
To avoid to include geochemical anomalies, outliers were deleted from the database of natural values. All the other values from levels below the modern enrichment were considered for BGV determination

$$\text{BGV} = \text{MNV} + 2s$$

	As (mg/kg)	Cd (mg/kg)	Cr (mg/kg)	Cu (mg/kg)	Hg (mg/kg)	Ni (mg/kg)	Pb (mg/kg)	Zn (mg/kg)
MNV	9.55	0.09	61.28	24.28	0.48	31.23	10.51	65.18
SD	3.62	0.03	15.62	5.63	0.19	9.76	3.55	15.52
BGV	16.78	0.16	92.51	35.54	0.87	50.75	17.60	96.22
Average shale (Turekian and Wedepohl, 1961)	13	0.3	90	45	0.4	68	20	95
Average upper crust (Li, 2000)	1.6	0.1	69	39	0.08	55	17	67
ERL (Long et al., 1995)	8.2	1.2	81	34	0.15	20.9	46.7	150
ERM (Long et al., 1995)	70	9.6	370	270	0.71	51.6	218	410

Hg = 0.87 mg/kg d.w.

THE ORBETELLO SITE – HG DISTRIBUTION ON SURFACE LAGOON SEDIMENT



Mercury distribution

Min value 0.05 mg/kg d.w.

Max value 20.05 mg/kg d.w.

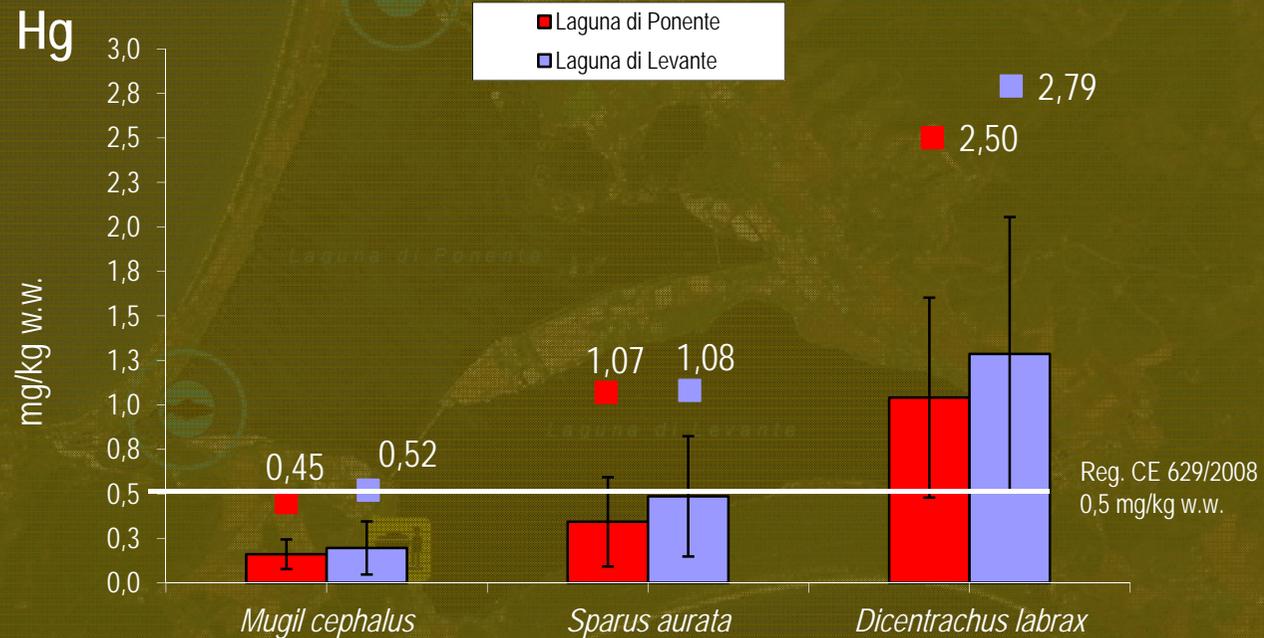
ORBETELLO SITE – HG LEVEL IN THE ORGANISMS

Sampled muscle fishes

Flathead mullet (*Mugil cephalus*)

Gilt-head bream (*Sparus aurata*)

European seabass (*Dicentrarchus labrax*)



 Fish sampling area

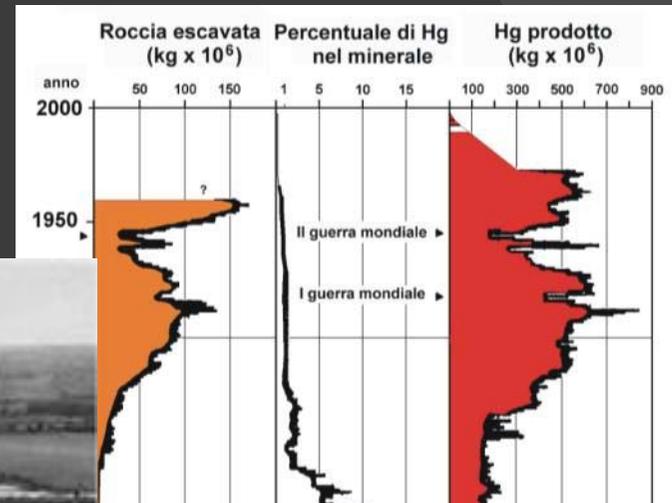
GRADO MARANO SITE

The Grado Marano lagoon is an area of natural interest. It's included in Community Interest Sites and Special Protection Zones - IT3320037 Laguna di Marano e Grado. It's characterized by shallow water separated by several waterways.

The main sediment supply is given by Isonzo river, whose mouth is located in the Trieste Gulf and which drain sediment Hg-enriched derives from the activity of Idrija mine, in Slovenia country. The sediments then are dispersed along the coast southwestward entering the lagoon mainly through East tidal inlet.

In the lagoon flow two important rivers, Aussa and Corno river, form the inner land. The first one collect the discharges of a chlor-alkali plant located in the north of the site, Torviscosa plant, not more active.

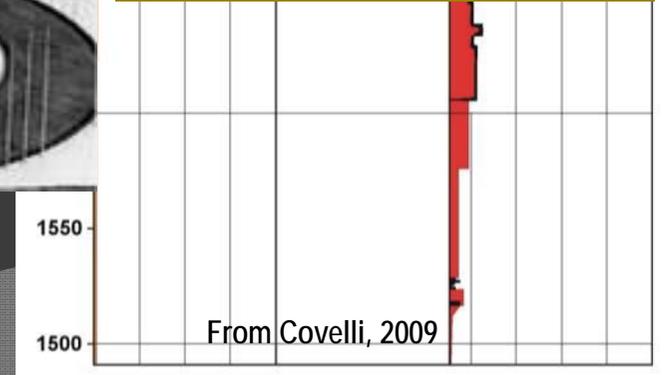




The Torviscosa chlor-alkaly plant has worked from 1950 until to early '90

The plant used 79 Hg-cells

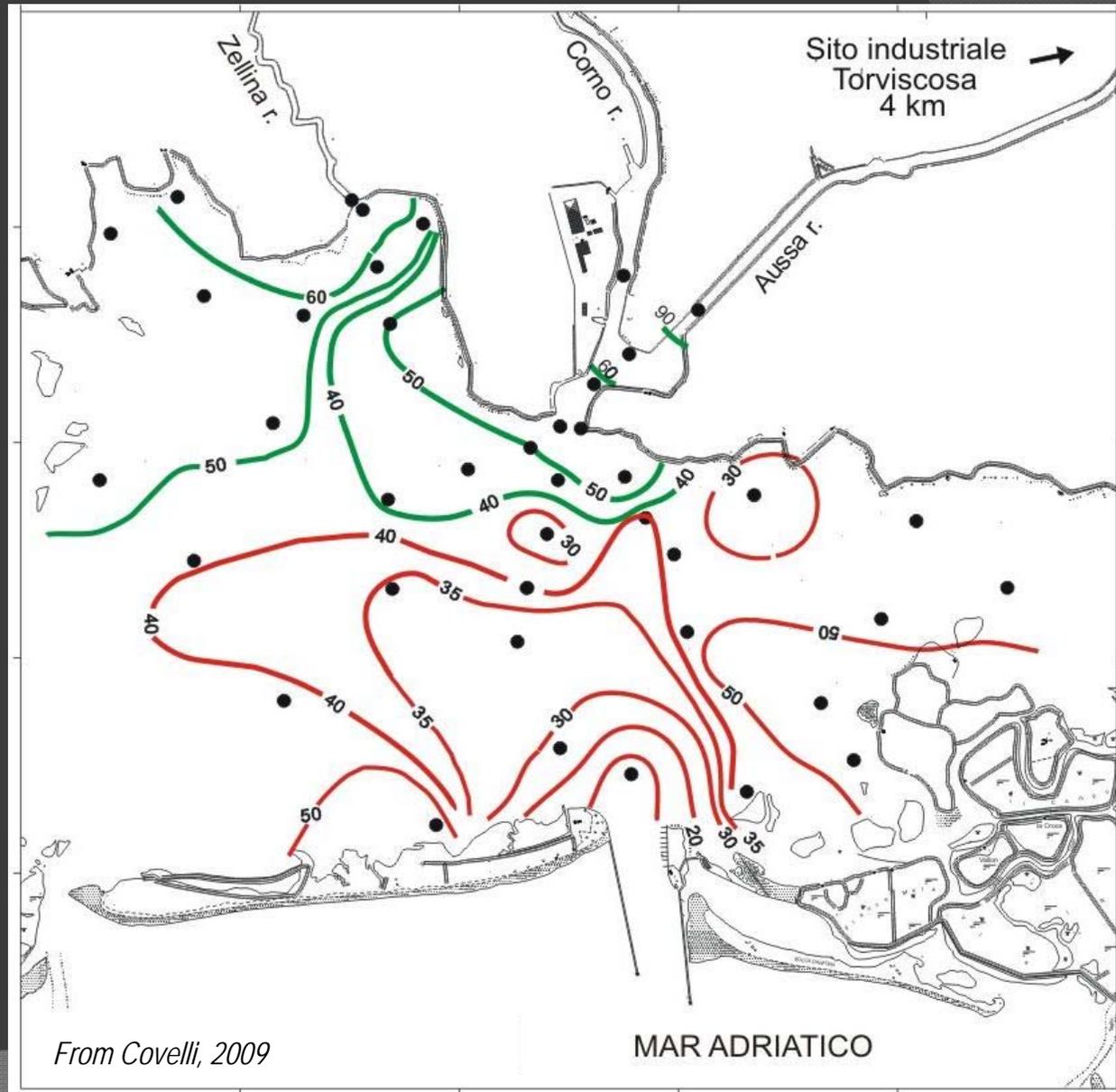
The discharge products polluted soil and groundwater and rivers for several years



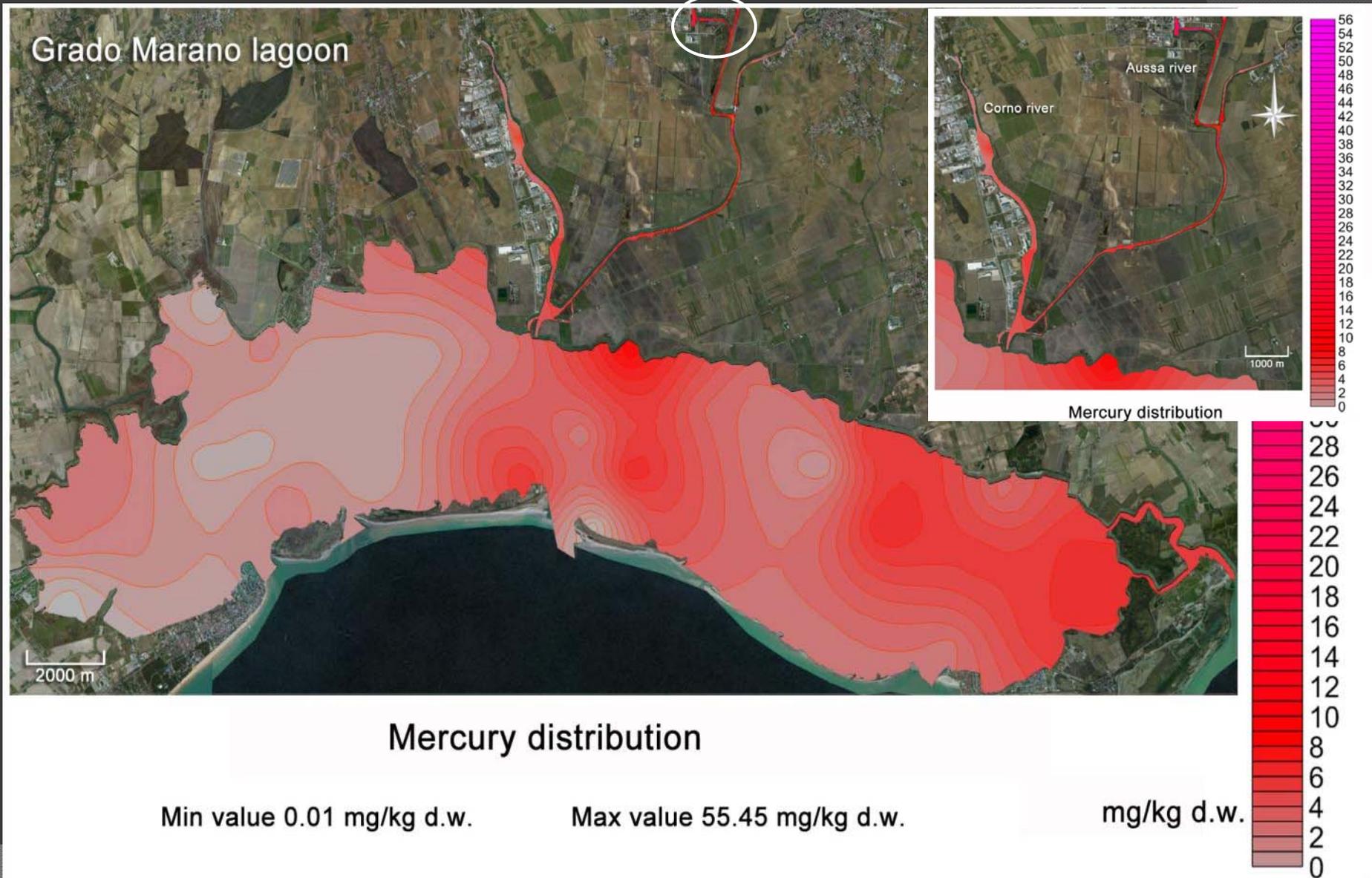
From Covelli, 2009

Influence of Isonzo and Aussa rivers in the distribution of the compounds of Hg in lagoonal sediments

-  *Aussa influence*
-  *Isonzo influence*



GRADO MARANO SITE – HG DISTRIBUTION ON SURFACE LAGOON SEDIMENT

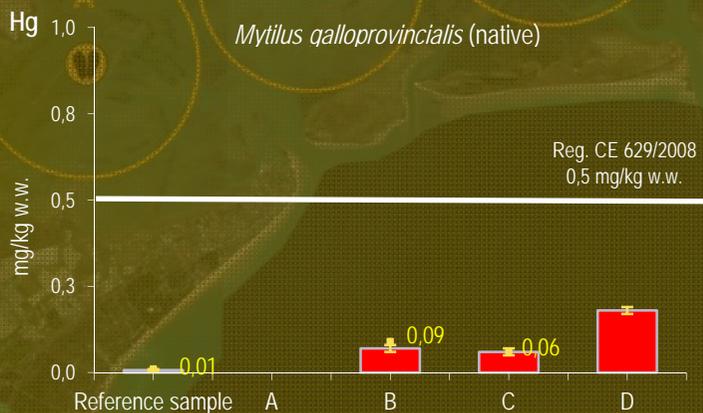
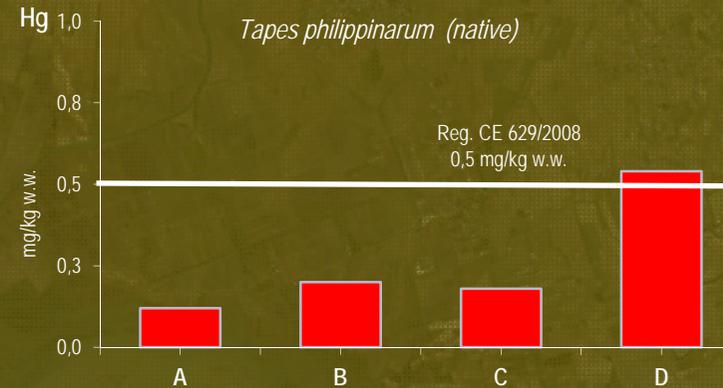
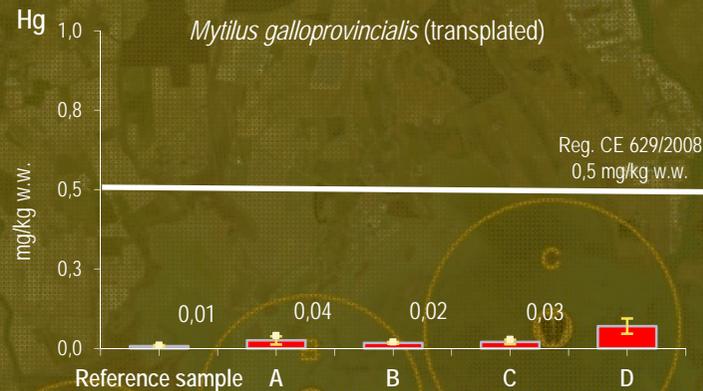
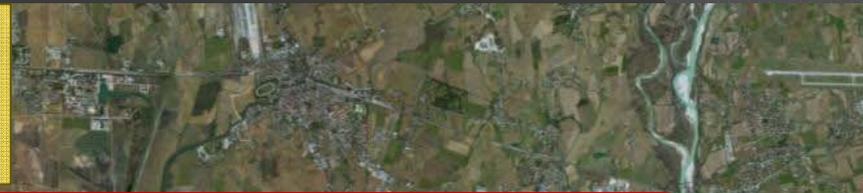


GRADO MARANO SITE – HG LEVEL IN THE ORGANISMS

Sampled muscle organisms

Mediterranean Mussel (*Mytilus galloprovincialis*) - native/transplated

Saltwater clam (*Tapes philippinarum*) - native



An higher level of bioaccumulation in the muscles of organisms collected in the Grado area were registered.

Saltwater clams registered, in the Grado area, higher values than CE regulation.

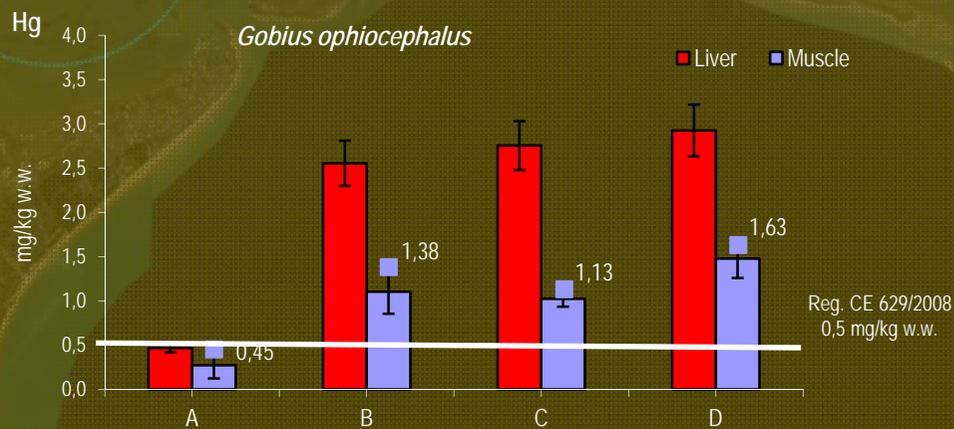
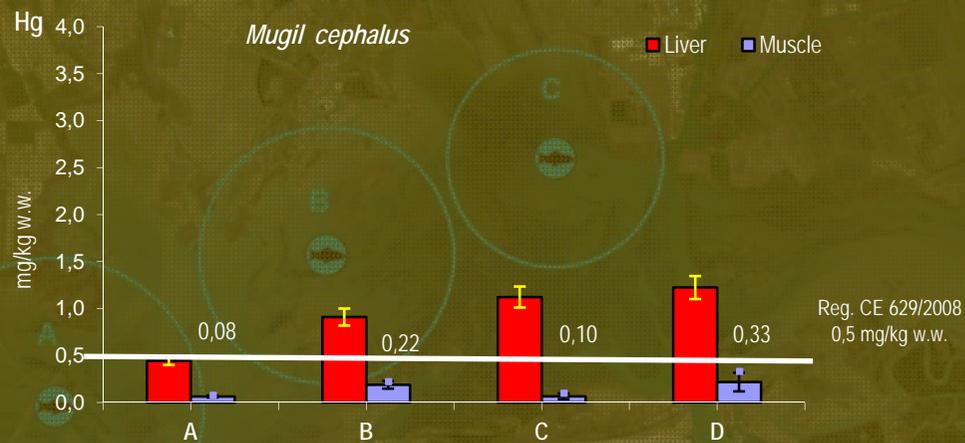
Transplated mussels show, in the Grado area, an higher trend to accumulation.

GRADO MARANO SITE – HG LEVEL IN THE ORGANISMS

Sampled fishes– liver/muscle

Flathead grey mullet (*Mugil cephalus*)

Grass goby (*Gobius ophiocephalus*)



An higher level of bioaccumulation in the liver, in comparison with muscle, of both sampled fishes were registered.

In all the areas, except for western one (site A) the Hg concentration in liver is higher than CE regulation for maximum levels of contaminant accepted for food. The same situation is observed for *Gobius* muscle

THE PRIOLO SITE

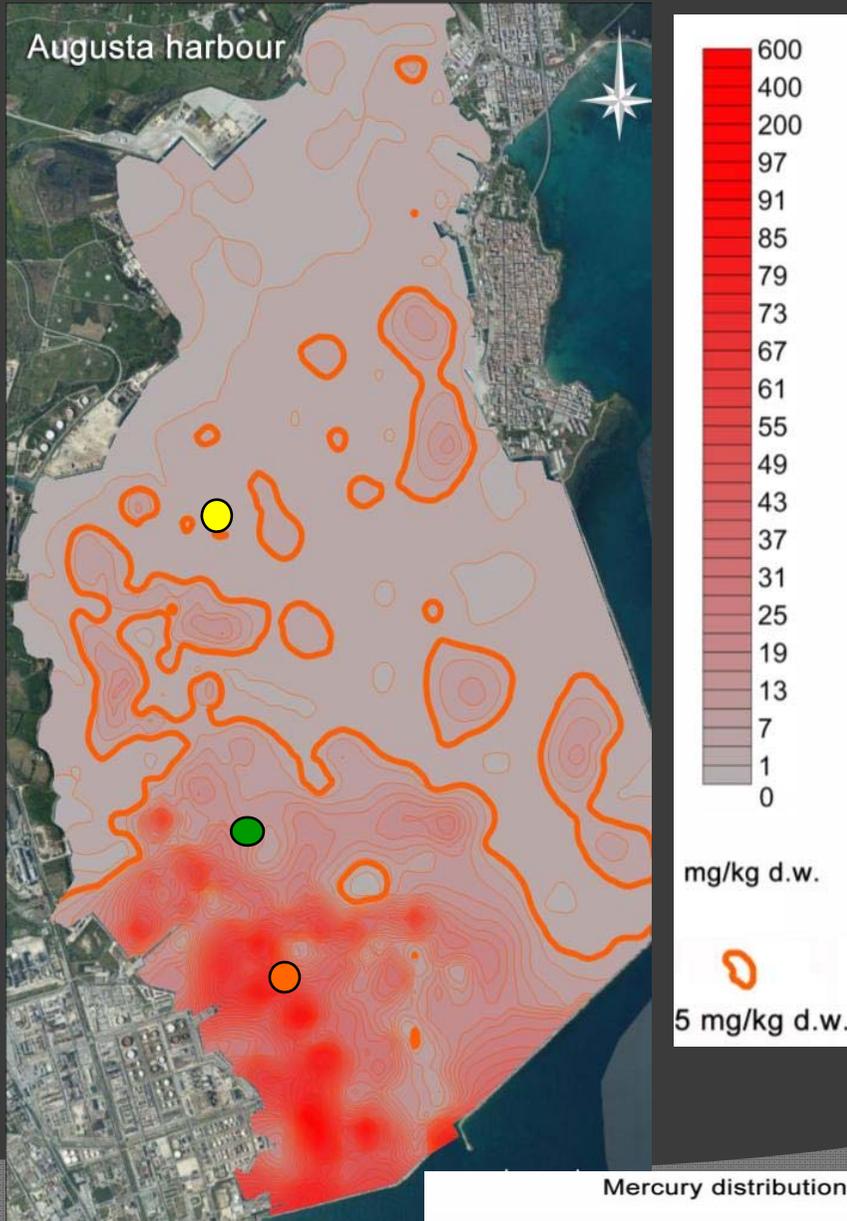


The Priolo site is affected by high anthropogenic impact due to a strong, past and still active, industrial activities. It's a very extensive area, including Augusta area, a natural bay closed by artificial dams in early '60. The water depth is deeper in correspondence with the main inlet and shallower water close to the coast where the hard substrate outcrops on the sea bottom. Water circulation is very weak and alternate the direction with different tide conditions.

The environmental status of marine area is highly influenced by past activity of klor-alkali plant, which was active from 1958 to 2003. Over 500 tonn of Hg was directly discharged in the sea from 1958 to 1979 through Vallone della Neve channel. In 2005 Hg-cells were removed.



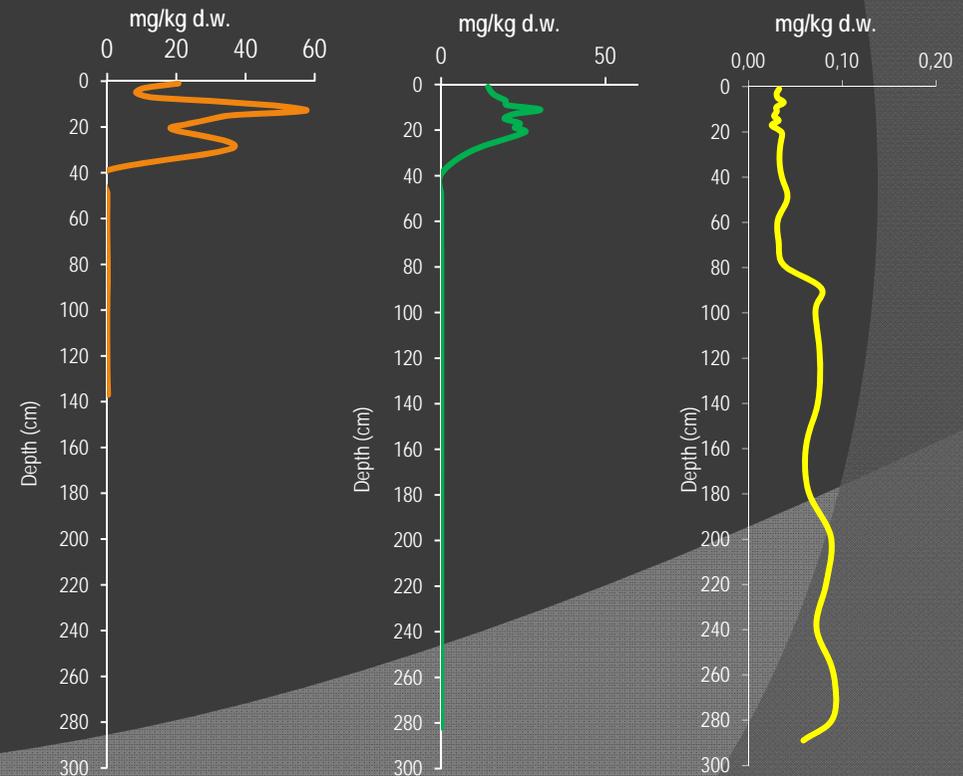
PRIOLO SITE – HG DISTRIBUTION ON SURFACE HARBOUR SEDIMENT



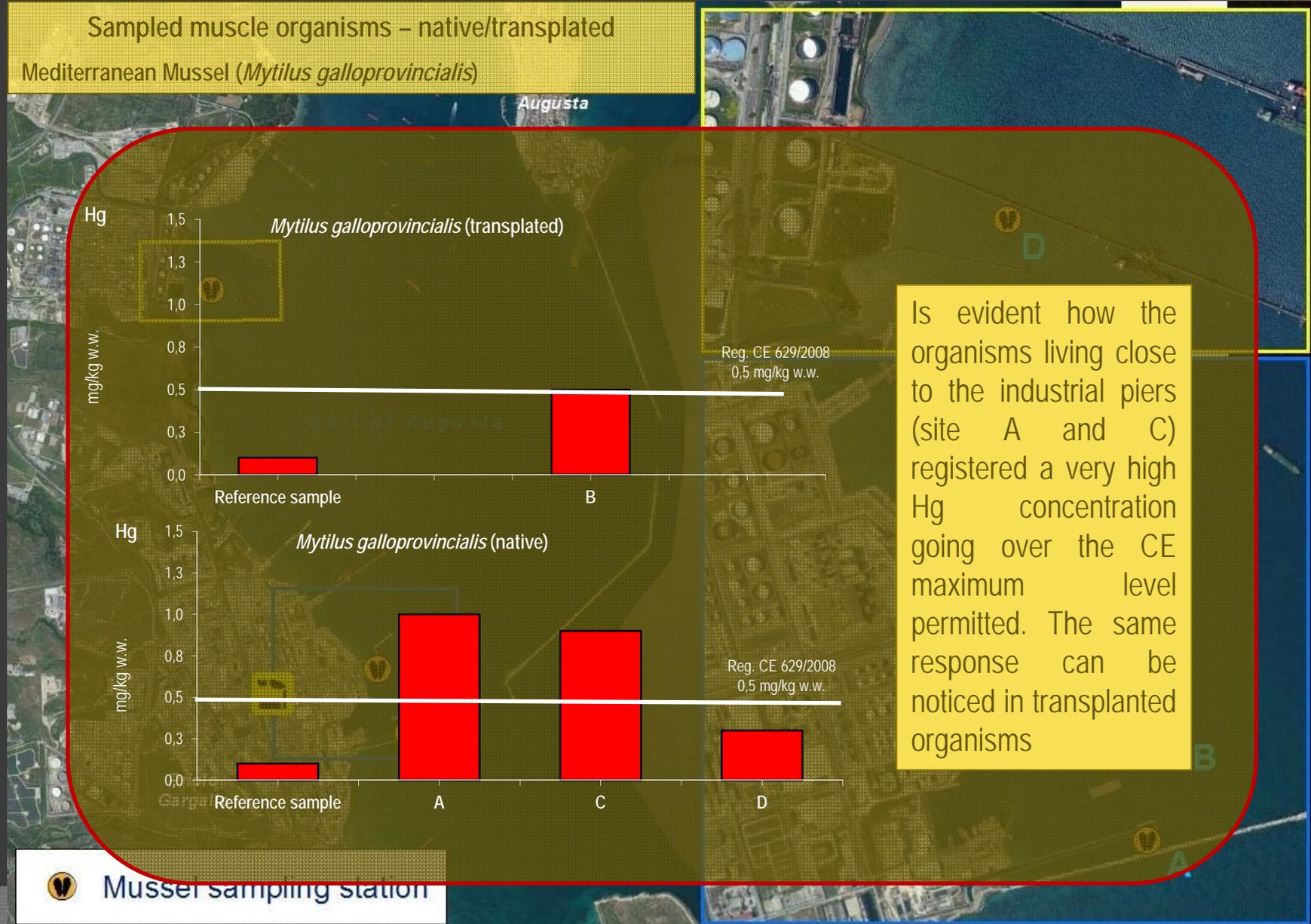
Min value 0 mg/kg d.w. Max value 527.35 mg/kg d.w.

The sediments of the southern area are highly polluted. The Hg contamination is also present in the deeper sediments (150 cm) with very high concentration (800 mg/kg d.w.), probably due to the active period of the plant.

A specific study demonstrated that Hg contamination move towards northern sector and around the harbour, thanks to water circulation and very fine sediments.



PRIOLO SITE – HG LEVEL IN THE ORGANISMS

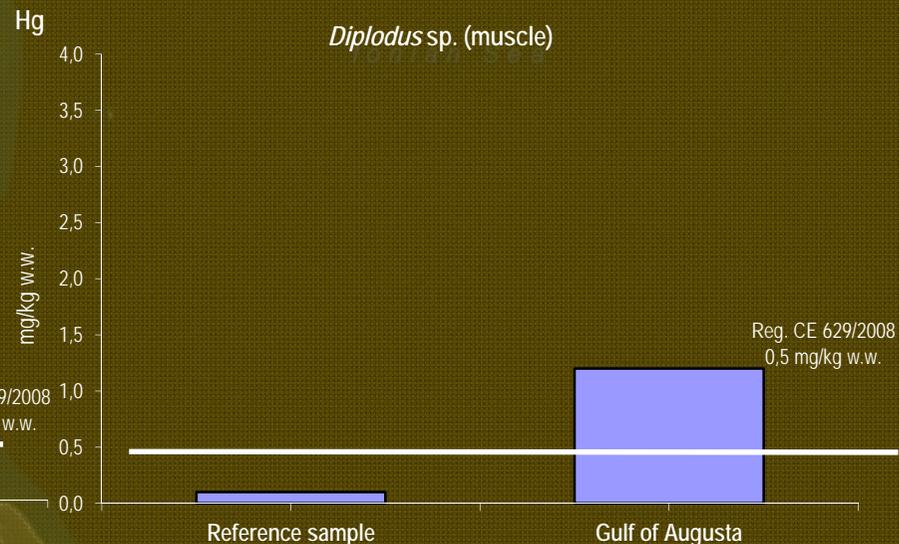
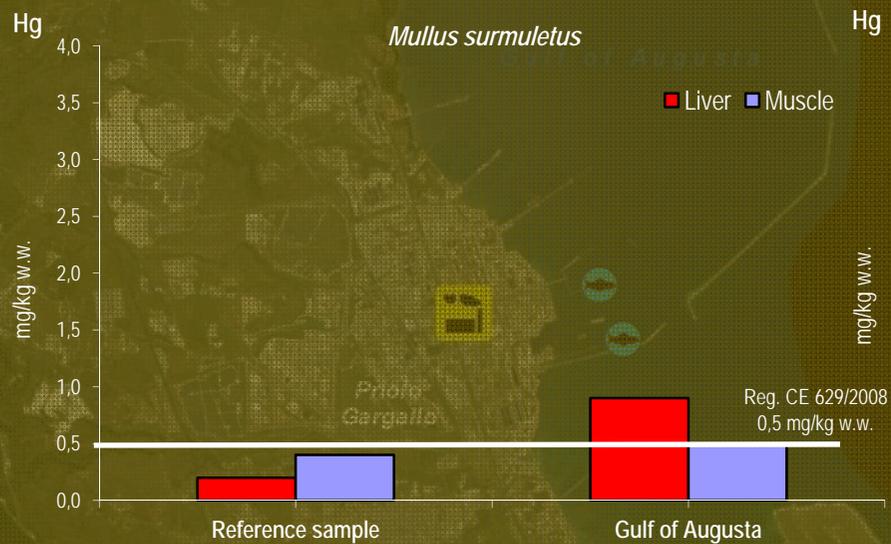


PRIOLO SITE – HG LEVEL IN THE ORGANISMS

Sampled muscle and liver organisms
Striped red mullet (*Mullus surmuletus*)
Sargo (*Diplodus* sp)

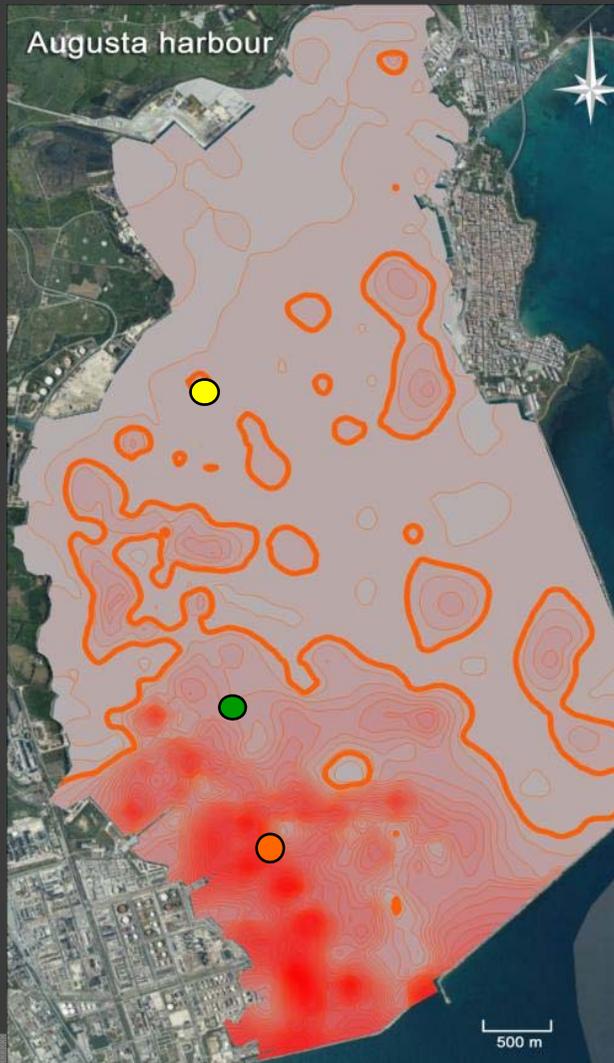


Hg concentration determined in sampled fishes point out the capacity of accumulation this contaminant both in their muscle and liver with levels higher than CE regulation.

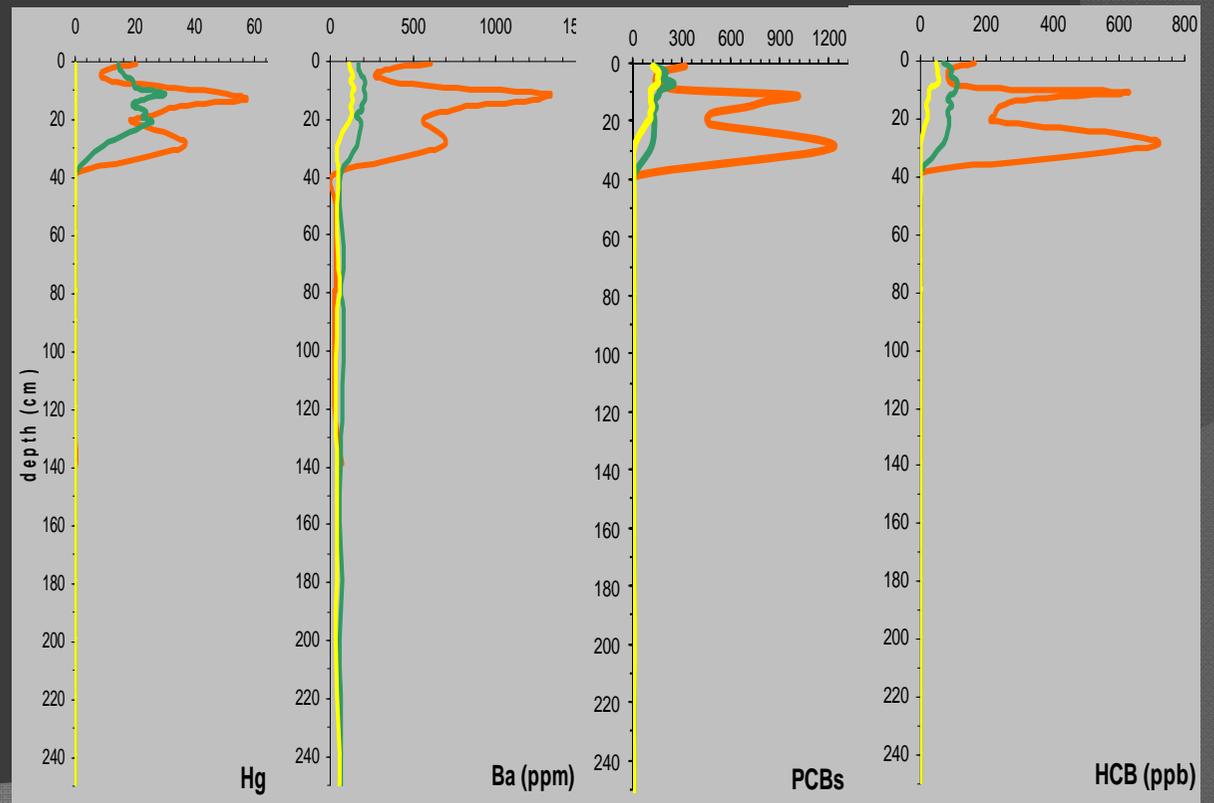


PRIOLO SITE – GEOCHRONOLOGICAL TOOLS

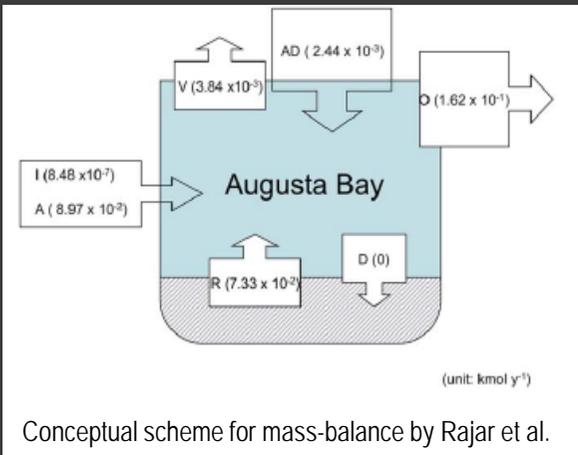
A geochronological study was carried out on sediment cores of the harbour to recognize the different contribution on pollution of different industries



A contamination due to Hg, Ba, PCBs and HCB was recognized. The strong correlation among these contaminants and their decreasing trend -from South to North- suggest a possible common "pollution source" in the southern harbour

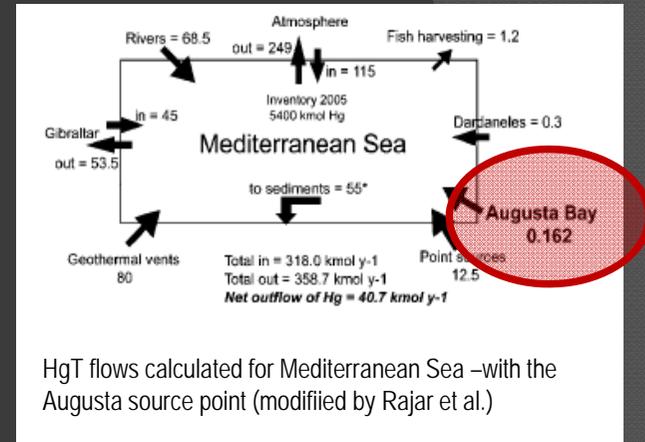


THE KEY ROLE PLAYED BY AUGUSTA HARBOUR IN THE HG CONTAMINATION OF THE MEDITERRANEAN SEA



$$I + A + AD + R = O + D + V$$

I = total Hg influx from the surface Mediterranean seawater
 A = inputs of dissolved Hg from anthropogenic activities
 AD = atmospheric Hg deposition
 R = Hg re-suspension/release from sediments
 O = total Hg outflow from the basin
 D = sedimentary deposition and burial
 V = evasion of HgT to the atmosphere



Augusta Bay results associated to the outflow of bottom waters that intercept surface meso-scale ocean circulation with potential widespread contaminant distribution effects at basin scale. Finally, the narrow continental margin off the Augusta coast, associated to steep slope and several gullies, creates preferential transfer routes for polluted sediments from the internal Augusta basin.

So, the potential release of HgT from contaminated sediments could certainly influence the HgT content of the Levantine Intermediate Waters with an effective mechanism of large-scale contamination of the entire Mediterranean basin.

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PAPER

The key role played by the Augusta basin (southern Italy) in the mercury contamination of the Mediterranean Sea

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Thank you for your attention!

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